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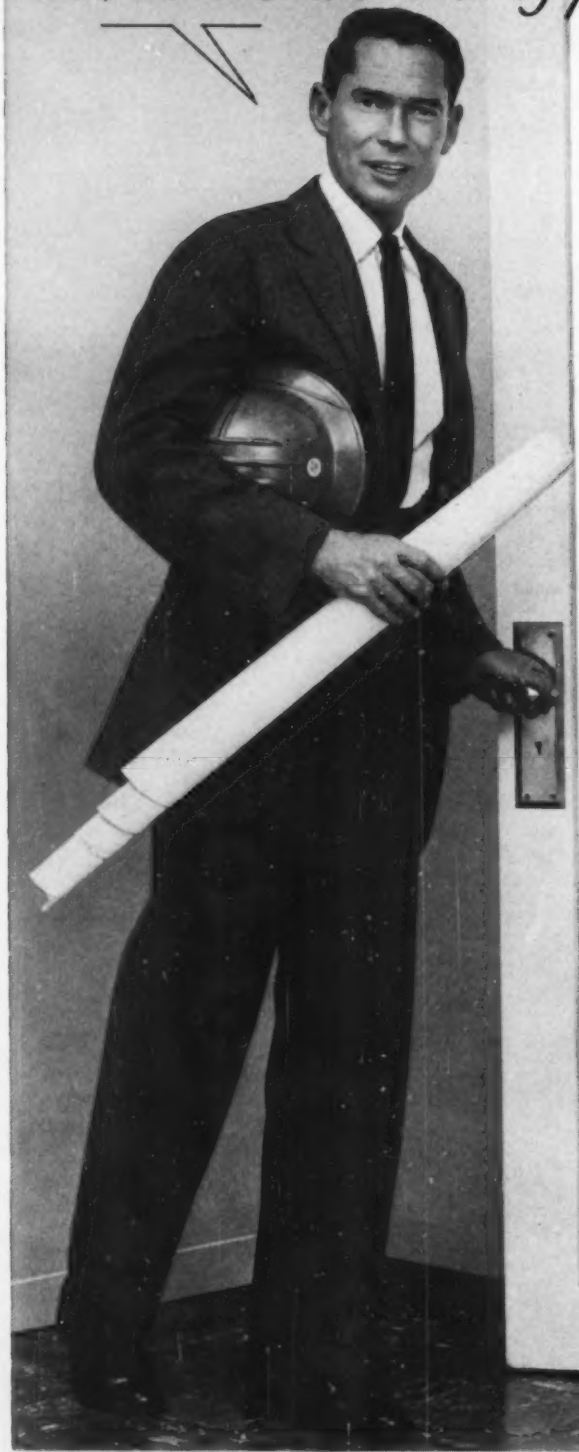

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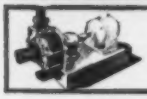

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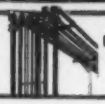

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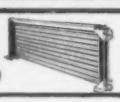

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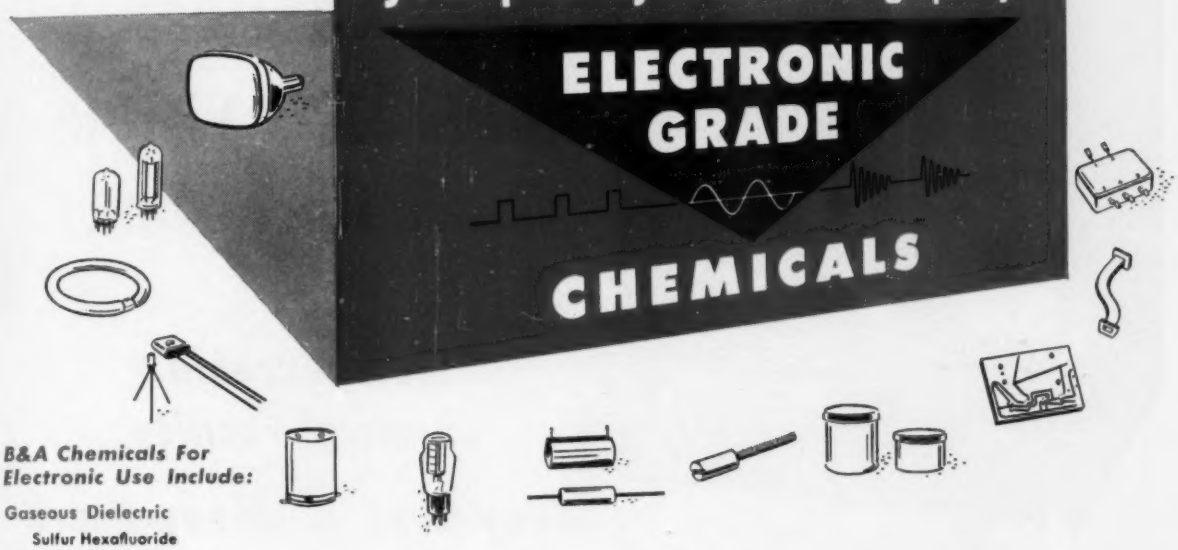

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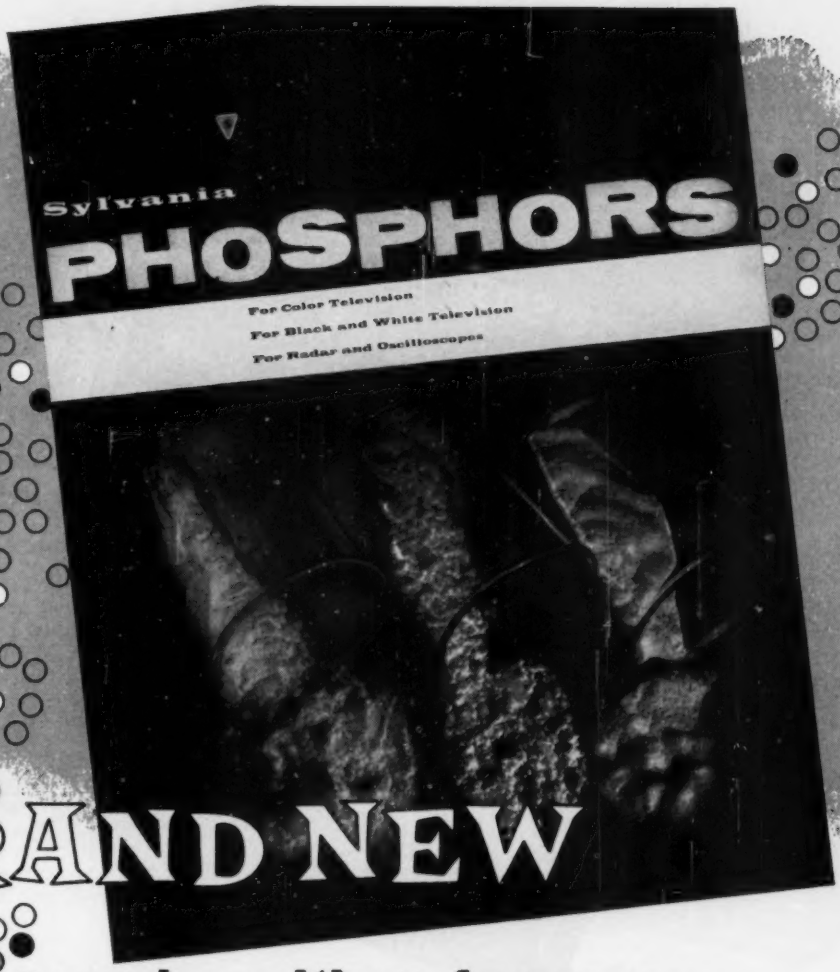

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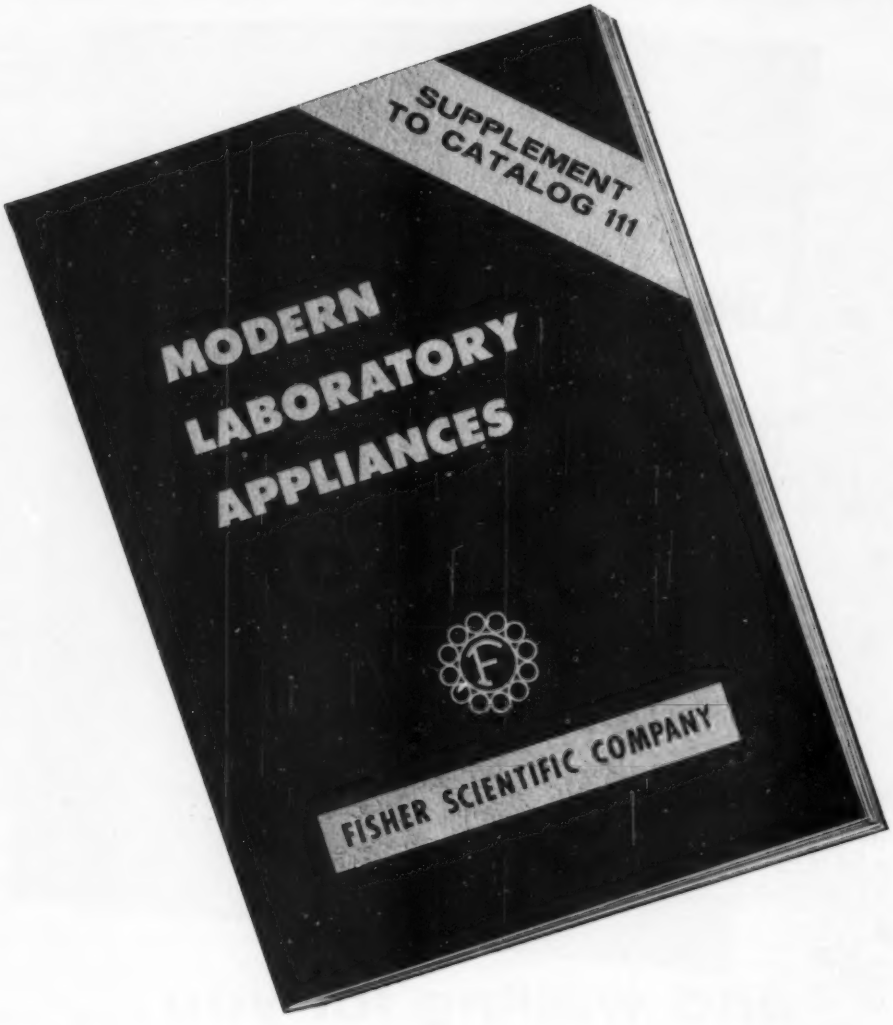

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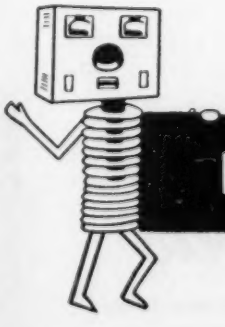

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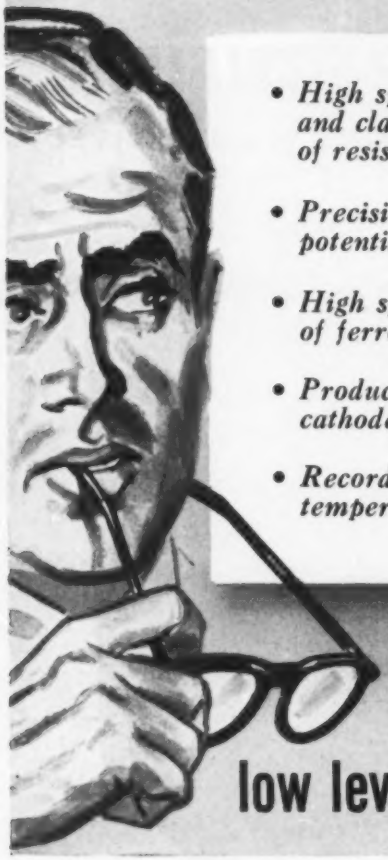

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Editorial

Future Plans and Policy

THE ELECTROCHEMICAL SOCIETY consists of some 2200 members, the organization our predecessors and we have built, and a certain amount of property and good will. About 10% of the members are affiliated with colleges and universities, the remainder with electrochemical industry, industrial research, and government laboratories. Our members understandably find association with the Society stimulating and profitable. Attendance at Society meetings has grown by leaps and bounds. The fact that nonmember attendance has recently exceeded that of members testifies to the interest and quality of the programs. It also indicates a fertile source of new members. Credit for these successful meetings must be given to the Division Chairmen and Executive Committees, who have given so much thought and effort to organization of the programs.

Your Editor cannot believe that the number of names on the membership list is truly indicative of the magnitude of the electrochemical industry, of the widespread interest and activity in various phases of the science, or of the present and potential value of our Society. At present somewhat more than 200 new members are admitted each year. For every five admitted, four drop out by resignation or simple default, and, of course, some members die. The net result is an increase of less than 2% per year. The Society must grow much faster if it is to represent the Science and the Industry adequately in the future, and, more mundanely, if it is to keep operational costs per member at a reasonable level. In a few years the Society may well need new and more expensive headquarters, and there is certainly pressure to increase the size of the JOURNAL. We hope and expect that dues and subscriptions need not be increased unduly.

Our Society President has pointed out that several areas of electrochemistry have in years past become absorbed in other fields of chemistry (H. H. Uhlig, Editorial, **102,** 103*C*, May 1955). This is easily understandable, and, at the same time, it presents a challenge to us. An obvious answer is to hold symposia in these related areas of electroanalysis, polarography, electrochromatography, study of fused salts and nonaqueous electrolytes, electrochemical thermodynamics, electrode kinetics, and the like. Our Society should pioneer in stimulating and publicizing new developments in such fields. Special symposia have played an important role in attracting nonmembers to Society meetings.

However, such symposia must be regarded with caution as a means of signing up new members. It is not very helpful to admit new members one year, only to have them resign the next because the Society has nothing further to offer them. Series of related symposia and inclusion of special-field material in all the regular programs and publications would seem better from the longer view of sustaining interest.

As Dr. Uhlig has said (*loc. cit.*), the Theoretical Division has an especially important responsibility. It can stimulate all the other Divisions, it is in the best position to attract academic nonmembers and students, it can try to foresee developments of future importance, it can discern the present and future VIP's in electrochemistry and add their names to the roster. If the Society gains prestige in its presentation and publication in all the important areas of theoretical electrochemistry, it need not fear lack of support from the "more practical" and industrial sectors.

Aside from the personal efforts of comparatively few individuals, a scientific society gains continuing prestige—and more members—through its publications. The monographs sponsored by the Society have proved highly successful. Subscriptions to the JOURNAL increase each year. This is extremely encouraging, because it means that school, corporation, and even public libraries find the JOURNAL in demand, and it is available to readers throughout much of the world. We believe that the quality of the JOURNAL is higher than ever before, and the present policy of including a larger number of technical articles in each issue should pay dividends in the long run. It is not easy to enlarge and improve the JOURNAL on a limited budget, but a wider appeal to readers is the sure way to gain more subscriptions and, in turn, to gain more contributions from the best authors. Any policy other than the greatest possible support to the JOURNAL can result only in flagging interest, resignations and withdrawals, and return to a smaller Society of more limited scope. —CVK

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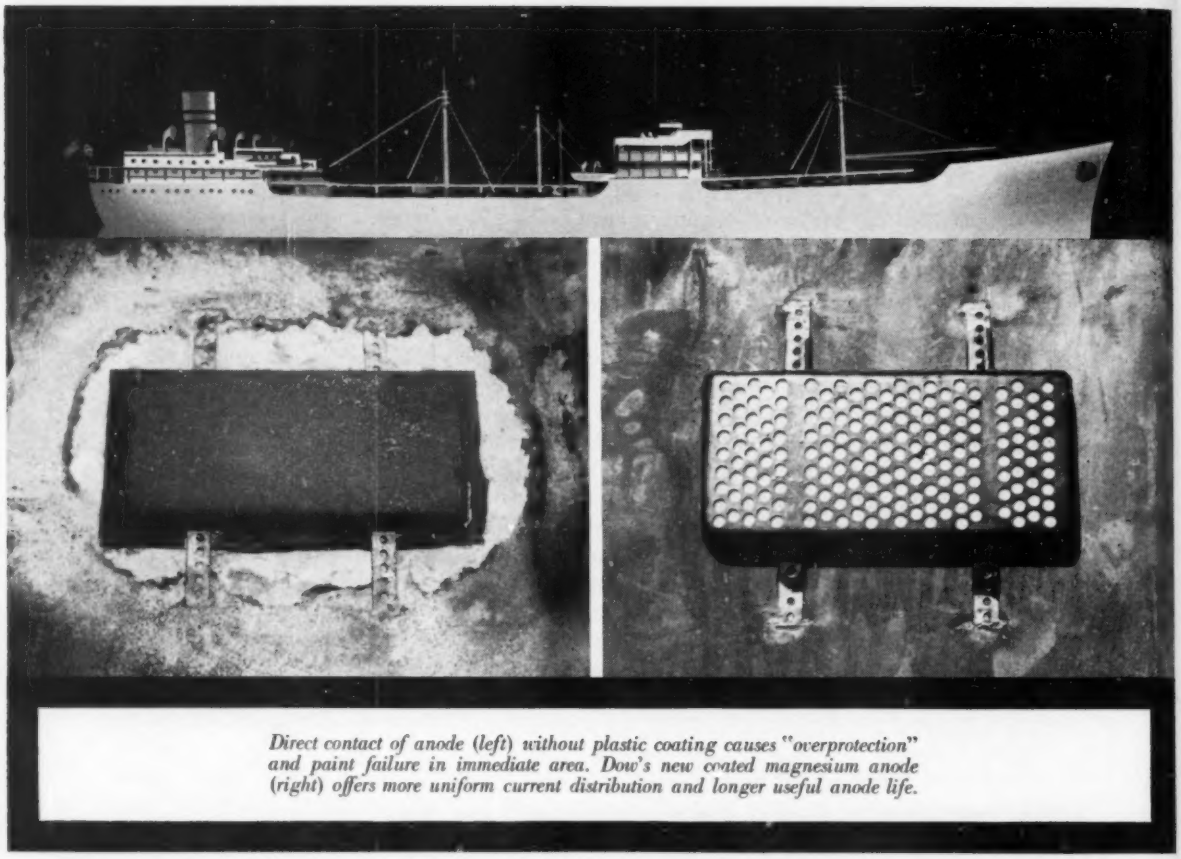

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Technical Review

The Lithium Industry

P. E. Landolt[1]

In recent years many articles have been published on lithium, so that reference to the literature will serve to acquaint those interested with the progress made in lithium technology and to justify the designation "Industry."

While the element lithium was discovered in 1807 by Arfvedsen in Sweden, little was done with it for nearly fifty years when Bunsen, Matthiesen, and others produced this element in metallic form. As early as 1817, Sir Humphrey Davy isolated a minute amount of metallic lithium.

With the advent of World War I, the Germans used lithium as a substitute material in lead bearings, "B-Metal," and in a light, strong aluminum alloy, "Scleron." In World War II lithium hydride was used principally as a source of hydrogen for air-borne sea-rescue work. After World War II interest in lithium and its compounds increased and a diverse number of uses followed: e.g., ceramics, pharmaceuticals, low temperature greases, air conditioning, metallurgical uses including fluxes for brazing and welding, alkaline storage batteries, etc.

Within the past few years, recognition of the stability of lithium hydride and of lithium isotope 6 as a source of tritium has made the element important in nuclear developments.

Growth of the Industry in the United States

Prior to World War II there was one principal producer of lithium products, Maywood Chemical Works, owning a rich source of raw materials in South Dakota and a chemical plant with a capacity of approximately 1,000,000 lb lithium carbonate per annum from which its various lithium products were made, including lithium metal.

During World War II, additional facilities were developed, increasing the over-all U. S. capacity to 4,000,000 lb lithium carbonate per annum. Prior to and during the war, American Potash and Chemical Corporation produced a by-product, lithium sodium phosphate, containing the equivalent of 1,000,000–1,500,000 lb per annum of lithium carbonate which was sold to Maywood Chemical Works and Foote Mineral Company. Immediately following the war, consumption of lithium products was reduced to the prewar figure of approximately 400,000–500,000 lb per annum (as carbonate).

This consumption steadily increased until it reached a figure of approximately 5,000,000 lb in 1954, with American Potash producing and selling its own lithium carbonate.

During 1954 Foote opened up and operated mining facilities at Kings Mountain, North Carolina, acquired from Solvay Division, Allied Chemical & Dye Corporation, and a new large chemical plant at Sunbright, Virginia.

Also during the past year, Lithium Corporation of America, in addition to its plant at St. Louis Park, Minnesota, completed a large plant adjacent to mining facilities at Bessemer City, North Carolina.

American Potash is now building a large plant at San Antonio, Texas, using raw materials from Northern Rhodesia.

Therefore, by the end of 1955, or certainly in 1956, there will be a total production capacity in the States of nearly 50,000,000 lb lithium carbonate or its equivalent per annum.

In 1955, it is expected that the consumption of lithium products will be of the order 12,000,000–15,000,000 lb (as carbonate), possibly more (see below).

The rest of the world, so far as it can be estimated, consumes less than 25% of this amount.

Raw Materials

Lithium occurs primarily in nature as complex aluminum silicates: spodumene $LiAl(SiO_3)_2$, lepidolite (a lithia mica), and petalite, a modified spodumene. It also occurs in lesser quantities as a fluophosphate, amblygonite $LiAlFPO_4$. It is also recovered from desert brines as a lithium sodium phosphate (20–22% Li_2O). The greatest quantities of lithium are recovered from spodumene.

Major Processes of Recovery

There are three principal methods practiced.

1. *Base exchange with alkali.*—This method was developed largely by Wadman[2] and von Girsewald.[3] In these methods ground spodumene or lepidolite is mixed with potassium sulfate or bisulfate (1:1) and heated to a high temperature (close to the fusion point). The mix is then cooled and leached to extract lithium sulfate and the excess potassium sulfate. This method is relatively expensive, being a batch operation and requiring potassium carbonate to precipitate lithium carbonate.

Similar methods using sodium sulfate have been suggested, but they are comparatively complicated and expensive.

2. *Roasting with lime.*—Spodumene concentrates mixed with CaO or $CaCO_3$ (1:2) are heated nearly to the fusion point. This reaction produces, after leaching, a solution of lithium hydroxide. Such methods are particularly attractive where lithium hydroxide is the desired end product. However, due to the limited solubility of lithium hydroxide, over-all recoveries of lithium are only fair.

A modification of this method was developed by Fraas and Ralston[4] in which a mix was prepared for portland cement manufacture, with lithium silicate minerals substituted for clay or shale, and to which $CaCl_2$ was added to convert and volatilize lithium as chloride.

This necessitated the simultaneous production of good cement clinker, free of alkali, and recovered the lithium as an impure chloride, very difficult to purify. It required operations of a magnitude great enough to produce cement competitively (at least 1000 bbl/24 hr). About 20% of the mix would be spodumene concentrates. It was never carried out on a commercial scale.

3. *Roasting with sulfuric acid.*—This process was developed by Ellestad and Leute.[5] Spodumene concentrates are first decrepitated at approximately 1100°C to convert alpha- to beta-spodumene. The material is then ground and mixed with

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[2] U. S. Pat. 847,856 (1906).

[3] U. S. Pat. 1,710,1556 (1929).

[4] U. S. Bureau of Mines RI 3344 (1937).

[5] U. S. Pat. 2,516,109 (1950).

H_2SO_4 (66°B) and heated to about 250°C. The material is then leached to extract lithium sulfate, which is then purified and treated with soda ash to precipitate and remove lithium carbonate.[6]

This method is being applied to the treatment of spodumene concentrates (4–6% Li_2O) and to mined ore (1–1.5% Li_2O).

Production of Lithium Metal (Electrolytic)

The starting materials for electrolysis are lithium chloride and potassium chloride. Various types of cells have been tried, but, in present practice, the type of cell developed for magnesium electrolysis is best adapted.

The cell is heated externally by gas or oil and the salt mixture (approximately a eutectic mixture) is fused. The anodes are graphite and the cathodes steel. Current is applied and molten lithium metal is formed, rising to the surface of the bath and collecting in an adjacent reservoir from which it is removed and cast in ingots, approximately 8.75 cm in diameter x 15 cm long (3.5 in. x 6 in.), weighing about 450 g (1 lb).

Chlorine forms at the anode and is vented from the cell and recovered. Five pounds of chlorine are produced for each pound of metallic lithium made. The bath temperature is approximately 550°C. About 20–22 kwh of electrical energy are required for each pound of lithium produced. Voltage required in the cell is 6–10 v. Multiple cells can be operated, reducing labor costs to a minimum.

Lithium Hydride Production

Lithium hydride is produced by introducing dry hydrogen into an autoclave (electrically heated) in which metallic lithium is placed. The reaction is carried on just above the melting point of the hydride, 630°C. Lithium hydride is a salt-like material, which when fused and electrolyzed releases hydrogen at the anode. Yields are close to theoretical values.

Lithium amide ($LiNH_2$) may be produced from lithium metal or lithium hydride, introducing ammonia into the reaction chamber held at a suitable temperature to produce the amide. Yields are close to theoretical values.

Research Outline for Lithium

One of the interesting factors in lithium developments is the large number of uses to which it may be put. These uses may be summarized as follows: ceramics; air conditioning; brazing and welding fluxes; all purpose lubricating greases; catalysis; metal refining and foundry operations; alloys; organic synthesis; pharmaceuticals; alkaline storage batteries; heat transfer; and nuclear phenomena.

This diverse use suggests possibilities of extended research in many of these fields. In fact, intensive research work is being carried on at present in many of these fields. Fundamental research on the properties of metallic lithium is also important, e.g., specific heats, conductivity, coefficient of expansion, etc.

Unique Properties of Lithium

Lithium has become important largely because of its unique properties. As an alkali element, it generally conforms to the expected properties of its group. However, it exhibits many properties that would appear to be more in common with the elements of the alkaline earth group; for example: lithium fluoride—insoluble in water; lithium carbonate—slightly soluble in water; lithium phosphate—insoluble in water; lithium hydroxide monohydrate—solubility 22 g in 100 g H_2O; lithium stearate—insoluble in water.

Lithium metal is extremely reactive: it combines with nitrogen, hydrogen, oxygen, sulfur, and several other elements.

Lithium and its ion are of especial interest to the electrochemist. The standard electrode potential (−3.02 v) is higher than that of any other metal, with the possible exception of cesium. In water the ion has exceptionally low mobility, in

TABLE I. *Consumption of lithium products (exact breakdown not available)*

	Annual demand in the U. S. (as equiv. Li_2CO_3)		Req'd raw material as 5% Li_2O concentrates (65% recovery)
	lb		*tons*
Prior to World War II	Min.	400,000	2,500
	Max.	750,000	4,700
World War II	Min.	2,000,000	12,500
	Max.	3,000,000	18,750
Postwar 1946–1950	Avg.	1,100,000	6,875
Expected demand—1955	In excess	10,000,000	62,500
1956–1960	In excess	30,000,000	187,500

TABLE II. *Growth of lithium metal consumption*

Prior to 1914	Experimental lots for research purposes
World production 1914–1942	Less than 5,000 lb/annum
U. S. 1942–1946	Less than 100,000 lb/annum
U. S. 1947–1952	Less than 30,000 lb/annum
U. S. 1955	Over 100,000 lb/annum
Potential demand	1,000,000± lb/annum

TABLE III. *Growth of industry capacity in the U.S. (as equiv. Li_2CO_3), in lb*

	1946	1954	1955	1956 Estimated
Lithium Corp. of America	3,000,000	3,000,000	12–15,000,000	20,000,000
Maywood Chemical Works	1,000,000 app.	1,000,000+	1,000,000	1,000,000
American Potash & Chemical Corp. est.	1,250,000 (jointly to Maywood and Foote Mineral Co.)	1,500,000	1,800,000	10,000,000
Foote Mineral Co. est.	1,000,000±	6,000,000	12–15,000,000	15,000,000
Total	5,000,000 app.	11,500,000	30,000,000	46,000,000

TABLE IV. *Consumption by use*

	1951 (as equiv. carbonate)		Est. 1955 (as equiv. carbonate)	
	000 lb	*%*	*000 lb*	*%*
Lubricating greases	816	27	3,300	39
Ceramics	779	26	1,600	19
Welding and brazing	287	9	1,100	13
Air conditioning	320	11	1,100	13
Alkaline storage	393	13	610	7
Pharmaceuticals	33	1	30	—
Defense and miscellaneous	393	13	760	9
	3,021	100	8,500	100

(*Chem. Week*, Nov. 8, 1952).

The 1955 consumption may be of the order of 20,000,000 lb Li_2CO_3 or its equivalent.

[6] See *Ind. Eng. Chem.*, **43**, 2636 (1951).

molten salts exceptionally high mobility. Lithium salts are used to lower the melting point and increase the fluidity of molten mixtures. The salts such as carbonate and chloride are quite stable at high temperatures.

Lithium has two isotopes in nature with mass numbers of 6 and 7 (approximate ratio 1 to 10). Radioactive Li^8 has a very short half-life. Lithium 6 is an interesting source of tritium (H^3), which is produced by slow neutron irradiation:

$$_3Li^6 + {}_0n^1 \rightarrow {}_2He^4 + {}_1H^3$$

Economics of Lithium

Production Statistics

Figures represented by the U. S. Bureau of Mines are presented on mined material. Some portion of such raw material, particularly lepidolite and petalite, is used directly in special glass manufacture. Tables I, II, III, and IV give information on consumption of lithium and growth of the industry.

Cost of Lithium Metal

The prime factor in the cost of lithium metal is in the raw material converted to useful salts. Therefore, if the cost of mineral concentrates necessary to ultimately produce lithium metal is known, it can be equated to the cost of metal as follows:

Raw material cost per unit Li_2O	Raw material cost/lb Li
@ $4.50	0.50
6.00	0.75
8.00	1.00
10.00	1.25
12.00	1.50

To this must be added the chemical extraction cost and the cost of producing lithium chloride. To these costs must be added labor, power, and maintenance for the production of metal, and depreciation, overhead, and profit. The price of the metal will be of the order of 10–15 times the raw material cost, depending on the output of metal produced.

Capital costs including working capital will be in the range of $5.00 to $8.00 per pound per annum production, including all operations from chemical extraction of the ore to metal.

SELECTED BIBLIOGRAPHY

P. Assmann, *Z. Metallkunde*, **18**, 256 (1926); *C. A.*, **20**, 1585, 3424 (1926).

A. Burckhardt, and G. Sachs, *Metallwirtschaft*, **11**, 239 (1932).

G. H. Chambers, and E. G. Enck, *Foote Prints*, **7**, No. 1, 1 (June 1934); *Chem. Ind.*, **34**, 405 (1934).

D. K. Crampton, *Trans. Am. Inst. Mining Met. Engrs.*, **104**, 164 (1933).

J. Czochralski and G. Welter, U. S. Pat. 1,620,081 and 1,620,082.

W. Frankenburger, *Z. Elektrochem.*, **32**, 481 (1926).

C. von Girsewald and H. Weidmann, German Pat. 413,721, U. S. Pat. 1,515,001.

J. A. Hedval, *Z. Elektrochem.*, **36**, 853 (1930).

F. Hess, U. S. Bureau of Mines R. I. 3040 (1938).

E. Koch, U. S. Pat. 1,926,545.

W. Kroll, German Pat. 537,716.

P. E. Landolt, *Mining Eng.*, **3**, 1045 (1951).

P. E. Landolt and F. R. Pyne, *Foundry*, **77**, 90 (1949).

P. E. Landolt, "Rare Metals Handbook," C. A. Hampel, Editor, Chap. 1, Reinhold Publishing Corp., New York (1954).

K. M. Leute and R. S. Ellestad, U. S. Pat. 2,516,109.

P. D. Frost, J. H. Jackson, A. C. Loonam, and C. H. Lorig, *J. Metals*, **188**, 1171 (1950).

G. Masing and G. Tammann, *Z. anorg. u. allgem. Chem.*, **67**, 183 (1910).

G. Masing and C. Hasse, *Wiss. Veröffentl.-Siemens-Korzern*, **7**, 321 (1928).

Metalloy Corp., Div. Lithium Corp. of America, Inc., Bibliography—Organo-lithium Compounds (1950), (1951), (1953).

H. Moissan, *Compt. rend.*, **135**, 652 (1902).

H. Osborg, *Trans. Electrochem. Soc.*, **66**, 91 (1934).

O. C. Ralston and F. Fraas, U. S. Bureau of Mines R. I. 3344 (1937).

E. E. Schumacher, W. C. Ellis, and J. F. Eckel, Bell Telephone System, Tech. Publ. B. 515, Oct. 1930.

W. C. Smith, U. S. Pat. 1,812,992; 1,812,993; 1,923,955.

P. F. Winternitz, U. S. Pat. 2,488,485.

A. L. De Sy, *Am. Foundryman*, **15**, 60 (1949); **15**, 838 (1949).

O. Smalley, *Iron Age*, **164**, 68 (1949).

The Electrochemical Thermodynamics of J. Willard Gibbs and the Stockholm Conventions

The Gibbs-Stockholm Electrode Potential

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ABSTRACT

The Stockholm Commissions (1953) of the I.U.P.A.C. have distinguished between the ambivalent half-cell emf (e.g., +0.76 v for a Zn anode; −0.76 v for a Zn cathode) and the sign invariant electrode potential (−0.76 v for a Zn electrode). The half-cell emf stems from the thermodynamics of Nernst, Lewis and Randall, and Latimer. It can be shown that the electrode potential has its thermodynamic foundation in the work of J. Willard Gibbs, and can be defined by his expression $V_m - V_s$ where "V_m, V_s denote the electrical potentials in pieces of the same kind of metal connected with..." the electrode m and the standard hydrogen electrode s, respectively. The electrode potential V ($= V_m - V_s$) remains sign invariant upon the reversal of an infinitesimal current flow, while the half-cell emf E changes sign. For the potential of a metallic electrode, Gibbs writes essentially $V_m - V_s = (Rt/n_m\mathbf{F}) \ln \gamma/G$, where γ is the density of the metal ions in solution, and G is analogous to Nernst's "metal solution pressure." In terms of the sign-invariant Gibbs-Stockholm electrode potential V, the free enthalpy is $\Delta\zeta = +n\mathbf{F}V$ for anodic oxidations and $\Delta\zeta = -n\mathbf{F}V$ for cathodic reductions.

Introduction

At the meeting of the International Union of Pure and Applied Chemistry held in Stockholm in 1953, the Commission on Physico-Chemical Symbols and Terminology and the Commission on Electrochemistry agreed to certain "Conventions Concerning the Signs of Electromotive Forces and Electrode Potentials" (1). With respect to whole cells, the Stockholm Commissions reaffirmed the familiar conventions promulgated by Lewis and Randall in 1923 (2).

With respect to *single electrodes*, however, the Stockholm Commissions went further than Lewis and Randall and established a distinction between the half-cell emf (of variable sign) and the electrode potential (of invariant sign). These two concepts had hitherto been used interchangeably by chemists and by engineers and had unfortunately led to the conflicting "American" and "European" conventions regarding the sign of the single electrode potential!

The half-cell emf E was originated by Nernst in 1889 (3), its thermodynamic properties were codified by Lewis and Randall (4) (under the name of "electrode potential"); in recent years it has been used extensively by Latimer (5) under the names of "half-reaction potential" or alternately of "oxidation potential" or "reduction potential." The half-cell emf E, with its ambivalent sign, is the "electrode potential" or "redox potential" taught to the great majority of American students by their textbooks of general, analytical, and physical chemistry.

The electrode potential, as defined by the Stockholm Commissions of 1953, seems to have been first adopted in 1911 in a tabulation of electrode potentials prepared by Abbegg, Auerbach, and Luther for the Deutsche Bunsen Gesellschaft (6). It was explicitly rejected by Lewis and Randall (4) who adhered to the older Nernst concept. As a result, the thermodynamic properties of the electrode potential have never been formally codified, it has been represented by a bewildering variety of symbols: π, Π, ψ, ϕ, or even E (which should be reserved for an electromotive force alone), its fundamental properties, notably that of sign-invariance, have been ignored or misunderstood in many American texts (7).

Yet, Gibbs' electrochemical thermodynamics (8), developed between 1875 and 1878 in his monumental paper "On the Equilibrium of Heterogeneous Substances," leads unambiguously to a potential, denoted by the symbol V, all of whose essential properties coincide with those of the Stockholm Commissions' electrode potential. For this reason, this potential might be referred to as the Gibbs-Stockholm electrode potential. However, the Stockholm Commissions refrained from assigning any symbols to the concepts defined by them. It seems safer, therefore, to refer to the potential V as the Gibbs electrode potential, keeping in mind the fact that the Gibbs electrode potential coincides in every fundamental respect with the Stockholm electrode potential.

It is the purpose of this paper to attempt a synthesis of the electrochemical thermodynamic conventions of Nernst, Lewis and Randall, and Latimer, together with those of the Stockholm Commissions of 1953, and with the thermodynamic treatment of Gibbs. It is perhaps not the least of the many paradoxes of electrochemistry that the "American" sign convention stemmed from the thermodynamics of Walter Nernst of Berlin while the "European" sign convention can find its thermodynamic foundation in the work of J. Willard Gibbs of New Haven. The Stockholm Conventions of 1953 have opened the door to a synthesis of the conflicting approaches. It is hoped that such a synthesis will enable all American chemists, theoretical as well as practical, to speak the same language in dealing with the potentials of electrodes.

The Whole-Cell EMF—The Conventions of Lewis and Randall and of the Stockholm Commissions

According to the convention of Lewis and Randall (2), the electromotive force E assigned to a given cell diagram, e.g.,

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Pt, H_2(g), HCl (a = 1), Cl_2(g), Pt; E^0_{298} = +1.3594 v (Ia)

Pt, H_2(g), HCl(0.1M), Cl_2(g), Pt; E_{298} = +1.4885 v (Ib)

"shall represent the tendency of the negative current to pass spontaneously through the cell from right to left," i.e., the electromotive force E measures the tendency of the whole-cell reaction

$$H_2 + Cl_2 = 2H^+ + 2Cl^- \quad \text{(II)}$$

[which accompanies the passage of negative electricity through cells (I) from right to left] to deliver electromotive work spontaneously to the external circuit. The Stockholm Commissions (1) have restated the above convention: "The electromotive force is equal in sign and magnitude to the electrical potential of the metallic conducting lead on the right when that of the similar lead on the left is taken as zero, the cell being open." The whole-cell reaction shall imply "a diagram so drawn that this reaction takes place when positive electricity flows through the cell from left to right. If this is the direction of the current when the cell is short-circuited, the electromotive force will be positive," as is the case for cells (I).

It should be noted that, in cells (I), the hydrogen electrode on the left is the anode[2] and the − terminal; the chlorine electrode on the right is the cathode and the + terminal.

In both the Lewis and Randall and in the Stockholm Commissions' Conventions, the reversal of the whole-cell reaction (i.e., the reversal of the direction of current flow) inverts the cell diagram and alters the sign of the electromotive force E, e.g.,

Pt, Cl_2(g), HCl(a = 1), H_2(g), Pt; E^0_{298} = −1.3594 v (IIIa)

Pt, Cl_2(g), HCl(0.1M), H_2(g), Pt; E_{298} = −1.4885 v (IIIb)

together with

$$2H^+ + 2Cl^- = H_2 + Cl_2 \quad \text{(IV)}$$

The inversion of the cell diagram is a requirement of convention only. But the change in the sign of the electromotive force E is a consequence of the Second Law of Thermodynamics. If the cell reaction (II) is capable of delivering electromotive work spontaneously (positive E value), cell reaction (IV) can occur only through the input of electromotive work from an external source (negative E value), as in the recharging of a battery. One can say that cell reaction (II) is galvanic, (IV) is electrolytic. Lewis and Randall (2) have emphasized "the importance of considering the electromotive force as a property, not of the cell, but of the reaction which occurs within the cell." It is not surprising, therefore, that E should change its sign as the reaction is reversed.

As regards the effect of a current reversal on the locus of the anode and cathode and of the + and − terminals, it is necessary to distinguish between the actual physical cell as mounted on a laboratory bench, and the conventional cell diagram as written on paper (7). In the physical cell, a current reversal interchanges the locus of the anode and cathode but leaves the + and − terminals unchanged. In the conventional cell diagram, the positive current is always considered to flow through the cell from left to right, the anode is always on the left, the cathode on the right; a current reversal inverts the cell diagram, and thereby inverts the polarities from the order −, + in a galvanic cell to +, − in an electrolytic cell. For example, in cells (I) and (III), the chlorine electrode is always the + terminal, the hydrogen electrode is always the − terminal, the anode is always on the left and the cathode on the right.

[2] The terms anode and cathode, in the minds of many American chemists, seem to mean the + and − electrodes, respectively. This is true enough in an electrolytic cell, but is completely wrong in a galvanic cell. This misapprehension seems to be due to the unsatisfactory manner in which these concepts are taught in most freshman chemistry courses. Michael Faraday (9) coined the terms anode and cathode to denote the surfaces at which the positive current enters and leaves the cell, respectively.

The Half-Cell EMF and the Stockholm Electrode Potential

There is no disagreement in the selection of the arbitrary zero point of the electrode potential scale, first proposed by Nernst (3). In Lewis and Randall's words (4): "We shall assume that the potential of hydrogen at atmospheric pressure, against an aqueous solution containing hydrogen ion at unit activity, is zero at all temperatures. This arbitrary assumption will make it possible to give numerical values to other single electrode potentials."

If a half-cell made up of an electrode and an electrolyte is represented by the expression: electrode, electrolyte, Lewis and Randall then say that, "the [half-cell emf][3] measures the tendency for negative electricity to pass from right to left, that is from the electrolyte to the electrode." If, on the other hand, the half-cell is expressed as: electrolyte, electrode, the half-cell emf[3] once again "measures the tendency of the negative current to pass from right to left. It has the same magnitude as before, but the opposite sign." Lewis and Randall add "it is also convenient to divide the total cell reaction into two electrode reactions (or half reactions) in which negative electricity appears as one of the substances in the chemical equation. Here also we decide by convention to write the equation for the electrode reaction in the direction in which it will occur when negative electricity passes from right to left through the junction in question."

The Stockholm Commissions have rephrased the above conventions as follows: "When we speak of the electromotive forces of the half-cells . . . Cl^-, Cl_2, Pt, . . . , we mean the electromotive forces on the cells . . . Pt, H_2, H^+ ‖ Cl^-, Cl_2, Pt . . . implying the reaction . . . $\frac{1}{2}H_2 + \frac{1}{2}Cl_2 = H^+ + Cl^-$ . . . where the electrode on the left is a standard hydrogen electrode. These electromotive forces may also be called relative electrode potentials or, in brief, *electrode potentials*."

"When on the other hand, we speak of the electromotive forces of the half-cells . . . Pt, Cl_2, Cl^- . . . , we mean the electromotive forces of the cells . . . Pt, Cl_2, Cl^- ‖ H^+, H_2, Pt . . . implying the reaction . . . $Cl^- + H^+ = \frac{1}{2}Cl_2 + \frac{1}{2}H_2$ . . . where the electrode on the right is a standard hydrogen electrode. These electromotive forces should *not* be called electrode potentials."

Granted Nernst's convention that E^0(Pt, H_2, H^+) = E^0(H^+, H_2, Pt) = 0.0000 v, the above set of conventions applied to cells (Ia) and (IIIa) and to the whole-cell reactions (II) and (IV) lead to the following expressions for the standard chlorine electrode:

$$2e^- + Cl_2 = 2Cl^-;\ E^0(Cl^-, Cl_2, Pt) = +1.3594 \text{ v} \quad \text{(V}a\text{)}$$

$$2Cl^- = Cl_2 + 2e^-;\ E^0(Pt, Cl_2, Cl^-) = -1.3594 \text{ v} \quad \text{(V}b\text{)}$$

The half-cell emf of the standard chlorine electrode can, therefore, have two values of opposite sign, as pointed out by Lewis

[3] Lewis and Randall used the terms "single potential" or "potential" at these points. The term "half-cell emf" has been substituted to conform with the nomenclature adopted by the Stockholm Commissions.

and Randall, depending on the orientation of the electrode diagram and the associated direction of the electrode reaction (and of the current flow).

As is the case with the whole-cell emf, the ambivalence of the half-cell emf is a necessary consequence of the Second Law of Thermodynamics. If a chlorine cathode (V*a*), coupled with a hydrogen anode, can spontaneously deliver electromotive work (positive E value), a chlorine anode (V*b*), coupled with a hydrogen cathode, can operate only through an input of electromotive work (negative E value). To paraphrase the words applied by Lewis and Randall to the whole-cell emf, one cannot emphasize too strongly the importance of considering the half-cell emf as a property, not of the electrode, but of the reaction which occurs at the electrode surface. A reversal of this reaction alters the sign of the half-cell emf.

The Stockholm Commissions have ruled that (V*a*) may be and that (V*b*) should *not* be called an electrode potential. Therefore, the standard electrode potential of the chlorine electrode has the value + 1.3594 v. It is unfortunate that most American chemists should have been brought up on electromotive series tables in which chlorine is consistently listed with the negative value (V*b*) which is *not* the electrode potential.

The Stockholm Commissions of 1953 have not explicitly developed the thermodynamic properties of the electrode potential, neither have they given it a distinct symbol. Both of these things can be done, however, by starting from the beautifully elegant thermodynamic formulation of electrochemical cells developed by Gibbs (8), a brief summary of which is given in the balance of this paper.

The Whole-Cell EMF—Gibbs' Notation

In Gibbs' treatment (8), the direction of the current, arbitrarily chosen, fixes the locus of the anode (′) and of the cathode (″). A current reversal interchanges these loci, e.g., in the hydrogen-chlorine cell, a galvanic current places the ″ on the chlorine; an electrolytic current places the ″ on the hydrogen. The symbols V' and V'' denote "the electrical potentials in pieces of the same kind of metal connected with the anode and cathode respectively." The potential difference $V'' - V'$ (or $V' - V''$) is experimentally measurable, e.g., by the use of a potentiometer. When the positive charge de is transferred from the metallic lead ′ through the cell to the metallic lead ″, the cell delivers the electromotive work $(V'' - V')de$ to the external circuit. The electromotive force is therefore $V'' - V'$ and this is equal to Lewis and Randall's E.

In the standard hydrogen-chlorine cell, the electromotive force of the galvanic reaction (II) is

$$(V'' - V')^0 = V^0(\mathrm{Pt, Cl_2, Cl^-}) - V^0(\mathrm{Pt, H_2, H^+}) = +1.3594 \text{ v} = E^0(\mathrm{I}a) \quad \text{(VI)}$$

while the electromotive force of the electrolytic reaction (IV) is

$$(V'' - V')^0 = V^0(\mathrm{Pt, H_2, H^+}) - V^0(\mathrm{Pt, Cl_2, Cl^-}) = -1.3594 \text{ v} = E^0(\mathrm{III}a) \quad \text{(VII)}$$

Thus, as in Lewis and Randall's and in the Stockholm Commissions' Conventions, the whole-cell emf[4] changes sign on a reversal of the current flow, in conformity with the requirements of the Second Law of Thermodynamics. If one accepts the Lewis and Randall and the Stockholm Conventions that a cell diagram shall always imply a flow of positive electricity through the cell from left to right, one may establish a correlation between their notations and Gibbs' by writing, for all cells,

$$V'' - V' = V(\text{cathode}) - V(\text{anode}) = V_{\text{right}} - V_{\text{left}} = E \quad \text{(VIII)}$$

Although the electromotive force $E = V'' - V'$ of the hydrogen-chlorine cell changes its sign upon the reversal of a current flow, the potential difference between the standard chlorine and standard hydrogen electrodes

$$V^0(\mathrm{Pt, Cl_2, Cl^-}) - V^0(\mathrm{Pt, H_2, H^+}) = +1.3594 \text{ v} \quad \text{(IX)}$$

remains sign-invariant when the current is reversed. A moment's reflection will show that this is true. Consider the standard hydrogen-chlorine cell (I*a*) or (III*a*) connected by two leads of the same kind of metal to a potentiometer. At the balance point, the potential difference (IX) is observed. The potentiometer can be thrown out of balance by an infinitesimal amount, and an infinitesimal current caused to flow in the direction of reaction (II) or of reaction (IV), without altering the observed potential difference (IX) by more than an infinitesimal amount from the value +1.3594 v.

The Gibbs Electrode Potential of the Standard Chlorine Electrode

If one accepts Nernst's choice of the zero of the potential scale, the potential difference (IX) can be taken as the definition of Gibbs' electrode potential of the standard chlorine electrode:

$$V^0(\mathrm{Pt, Cl_2, Cl^-}) = +1.3594 \text{ v} \quad \text{(X}a\text{)}$$

Since the potential difference (IX) remains sign invariant when an infinitesimal current is reversed, one may write indifferently

$$V^0(\mathrm{Pt, Cl_2, Cl^-}) = V^0(\mathrm{Cl^-, Cl_2, Pt}) = +1.3594 \text{ v} \quad \text{(X}b\text{)}$$

A comparison with the half-cell emf's (V) leads to the following array of values:

Electrode	Half-Reaction	E^0	V^0
Cl^-, Cl_2, Pt	$2e^- + Cl_2 = 2Cl^-$	+1.3594	+1.3594
Pt, Cl_2, Cl^-	$2Cl^- = Cl_2 + 2e^-$	−1.3594	+1.3594

This tabulation emphasizes once again the fact that the half-cell emf, as a measure of the electromotive work available in a given half-reaction, changes its sign when the half-reaction is reversed; the electrode potential, as a property of the electrode at which the two half-reactions are in equilibrium, remains sign-invariant. It also completes the proof that the Gibbs electrode potential V coincides with the Stockholm electrode potential.

The Electrochemical Law of Mass Action

The E values given for cells (I*b*) and (III*b*) indicate that a change in chemical activity or chemical potential alters the value of the electromotive force of a cell. This effect can be handled by the well-known chemical thermodynamic methods of Gibbs, Nernst, and Lewis and Randall.

Gibbs developed the thermodynamics of electrochemical cells by two different approaches. His first approach,[5] re-

[4] Gibbs also introduces the concept, widely used in practical electrochemistry, of the "external electromotive force $V' - V''$ applied to an electrolytic combination." The emf $V' - V''$ is positive for an electrolytic current.

[5] "On the Equilibrium of Heterogeneous Substances," pp. 332-333.

stricted in application to electrode concentration cells, leads essentially to the equation

$$V'' - V' = -(\mu_i'' - \mu_i')/z_i\mathbf{F} \qquad \text{(XI)}$$

for the electromotive force of a cell consisting of two electrodes reversible to the electrolysis of the substance i, in a solution of uniform composition through which i can be transferred as an ion, z_i is the valence (with sign), $\mathbf{F}$ the faraday, and μ_i', μ_i'' the (chemical) potentials (per mole) of i in or at the two electrodes. As examples of cells to which equation (XI) could be applied, Gibbs mentions Zn, $ZnSO_4$, Zn (in Hg); Pd, $H_2(\mu')$, H_2SO_4, $H_2(\mu'')$, Pd. Still another cell would be Pt, $Cl_2(\mu')$, HCl, $Cl_2(\mu'')$, Pt. Gibbs adds this remark: "the greater [chemical] potential of an anion [i.e., of a substance transferred through the cell as an anion]" occurs "at the same electrode as the greater electrical potential, . . . the reverse being true of a cation."

Gibbs' second approach[6] is of general applicability to all reversible cells and also to irreversible cells maintained at constant and uniform temperature. The electromotive work done by the cell is written in the form

$$(V'' - V')de = -d\epsilon + dQ + dW_G + dW_P \leqq -d\epsilon + td\eta + dW_G + dW_P \qquad \text{(XII)}$$

where $-d\epsilon$ is the intrinsic energy drop of the cell, dQ the heat received from external bodies, dW_G and dW_P the work received by the cell from gravity and from the external pressures, respectively, t the absolute temperature, and $d\eta$ the entropy gain of the cell. In a cell of ordinary dimensions, the work done by gravity and the pressure differences between different parts of the cell may be neglected. Let Gibbs' fundamental function ζ be defined as $\epsilon - t\eta + pv$ (this is Lewis and Randall's "free energy" F; in this paper, it will be called the free enthalpy).[7] If the pressure as well as the temperature is maintained uniform and constant, one can write $d\zeta = d\epsilon - td\eta + pdv$ and $dW_P = -pdv$. Therefore, equation (XII) gives for the electromotive force

$$V'' - V' \leqq -d\zeta/de \qquad \text{(XIII)}$$

For reversible cells, equation (XIII) takes the more familiar form

$$V'' - V' = E = -\Delta\zeta/n\mathbf{F} \qquad \text{(XIV)}$$

where n is the number of faradays transferred for one unit of the cell reaction whose free enthalpy drop[8] is $-\Delta\zeta$. The inequality in (XIII) applies to irreversible cells, where the difference between the two sides is known as the polarization potential. Expression (XIII) applies equally well to electrolytic cells. This is perhaps best seen after multiplication by $-de$

$$(V' - V'')de \geqq d\zeta \qquad \text{(XIII}a\text{)}$$

$(V' - V'')de$ is the electromotive work supplied to the cell, $d\zeta$ its free enthalpy gain.

The application of equations (XI) and (XIV) to mass action effects on emf and on potential can be done by the use of two well-known equations of chemical thermodynamics, i.e., Gibbs' equation

$$\zeta = n_1\mu_1 + n_2\mu_2 + n_3\mu_3 + \cdots \qquad \text{(XV)}$$

and Lewis' equation

$$\mu_i = \mu_i^0 + Rt \ln a_i \qquad \text{(XVI)}$$

where $n_1, n_2, n_3, \cdots$ represent the mole numbers of substances $1, 2, 3, \cdots$, μ_i^0 is the standard chemical potential (per mole), R is the universal gas constant ($R = 0.0862$ and $2.3026R = 0.1984$ expressed in millivolt-faradays per mole-deg K; $Rt = 25.69$ and $2.3026Rt = 59.16$ expressed in millivolt-faradays per mole, at $t = 298°K$), and a_i is the (chemical) activity of substance i which (apart from a correction factor of order of magnitude unity called the activity coefficient) can be taken as proportional to the concentration or density of i.

The Gibbs Electrode Potential of a General Electrode

Consider the three cells

$$\text{Pt}', \text{S.H.E.} \parallel \text{Zn}^{++}, \text{Zn}, \text{Pt}'' \qquad \text{(XVII}a\text{)}$$

$$\text{Pt}', \text{S.H.E.} \parallel \text{H}^+, \text{H}_2, \text{Pt}'' \qquad \text{(XVII}b\text{)}$$

$$\text{Pt}', \text{S.H.E.} \parallel \text{Cl}^-, \text{Cl}_2, \text{Pt}'' \qquad \text{(XVII}c\text{)}$$

where the left-hand electrode is a standard hydrogen electrode and the double bar means that the liquid junction potential, if any, has been either eliminated or minimized to the desired degree, the measured emf $V'' - V'$ may be taken as defining the Gibbs electrode potential of the three right-hand electrodes.

The corresponding half-cell reactions are, at the S.H.E.: $H_2(a = 1) = 2H^+(a = 1) + 2e^-$ (for which $V^0 = E^0 = 0$, and $-\Delta\zeta^0 = 0$ by Nernst's convention); and, at the three right-hand electrodes:

$$\text{Zn}^{++} + 2e^- = \text{Zn} \qquad \text{(XVIII}a\text{)}$$

$$\text{H}^+ + e^- = \tfrac{1}{2}\text{H}_2 \qquad \text{(XVIII}b\text{)}$$

$$\text{Cl}_2 + 2e^- = 2\text{Cl}^- \qquad \text{(XVIII}c\text{)}$$

The free enthalpy drop of these three half-cell reactions determines the emf of the entire cell and therefore the Gibbs electrode potential of the corresponding electrodes. These three *free enthalpy drops* may be expressed by

$$-\Delta\zeta = \mu(\text{Zn}^{++}) - \mu(\text{Zn}) \qquad \text{(XIX}a\text{)}$$

$$-\Delta\zeta = \mu(\text{H}^+) - \tfrac{1}{2}\mu(\text{H}_2) \qquad \text{(XIX}b\text{)}$$

$$-\Delta\zeta = \mu(\text{Cl}_2) - 2\mu(\text{Cl}^-) \qquad \text{(XIX}c\text{)}$$

By substitution of (XVI) and (XIX) into (XIV), keeping in mind the fact that the sign-invariant V is the same for Zn^{++}, Zn and for Zn, Zn^{++}, the Gibbs electrode potentials[9]

[6] See footnote 5, pp. 338–339, 348–349.

[7] It is only in recent years that a systematic nomenclature has come into being to designate Gibbs' four fundamental functions: ϵ as the energy, ψ as the free energy, χ as the enthalpy, and ζ as the free enthalpy. ψ is the "free energy" of Helmholtz; ζ the "free energy" of Lewis and Randall. All four fundamental functions are "work functions" (notwithstanding the fact that this term has usually been applied only to ψ), e.g., in an adiathermal process (such as the expansion of steam in an engine), the maximum total work is given by the energy drop, the maximum useful work by the enthalpy drop; in an isothermal process (such as the discharge of a battery), the maximum total work is given by the free energy drop, the maximum useful work by the free enthalpy drop.

[8] The free enthalpy drop is equal to the thermodynamic affinity of DeDonder and Van Rysselberghe (10).

[9] Guggenheim (11) has shown that Gibbs' electrode potentials for single electrodes of the type of (XXa), (XXb), and (XXc), when taken by themselves, have no meaning, because they involve unmeasurable single ion activities. However, any linear combination of Gibbs' electrode potentials, in which the product of the single ion activities gives the activity of a neutral electrolyte, becomes meaningful and represents a potential difference that is measurable. Single electrode potentials of the type of (XXa), (XXb), and (XXc) can be made meaningful in the approximately valid (and very widely

are obtained in the form[10]

$$V'' - V' = V(\mathrm{Zn}, \mathrm{Zn}^{++}) = V^0(\mathrm{Zn}, \mathrm{Zn}^{++}) + (Rt/2\mathbf{F}) \ln (\mathrm{Zn}^{++})/(\mathrm{Zn}) \quad (XXa)$$

$$V'' - V' = V(\mathrm{Pt}, \mathrm{H}_2, \mathrm{H}^+) = V^0(\mathrm{Pt}, \mathrm{H}_2, \mathrm{H}^+) + (Rt/\mathbf{F}) \ln (\mathrm{H}^+)/(\mathrm{H}_2)^{1/2} \quad (XXb)$$

$$V'' - V' = V(\mathrm{Pt}, \mathrm{Cl}_2, \mathrm{Cl}^-) = V^0(\mathrm{Pt}, \mathrm{Cl}_2, \mathrm{Cl}^-) + (Rt/2\mathbf{F}) \ln (\mathrm{Cl}_2)/(\mathrm{Cl}^-)^2 \quad (XXc)$$

where the symbol (Zn^{++}) denotes the activity of zinc ions, and the Gibbs standard potentials are

$$V^0(\mathrm{Zn}, \mathrm{Zn}^{++}) = [\mu^0(\mathrm{Zn}^{++}) - \mu^0(\mathrm{Zn})]/2\mathbf{F} = -0.763 \text{ v} \quad (XXIa)$$

$$V^0(\mathrm{Pt}, \mathrm{H}_2, \mathrm{H}^+) = [\mu^0(\mathrm{H}^+) - \tfrac{1}{2}\mu^0(\mathrm{H}_2)]/\mathbf{F} = 0.0000 \text{ v} \quad (XXIb)$$

$$V^0(\mathrm{Pt}, \mathrm{Cl_2Cl}^-) = [\mu^0(\mathrm{Cl}_2) - 2\mu^0(\mathrm{Cl}^-)]/2\mathbf{F} = +1.3594 \text{ v} \quad (XXIc)$$

on the activity scales recommended by Lewis and Randall[1] (14). For a generalized half-cell reaction, $Ox + ne^- = Red$, the Gibbs electrode potential may be written in the form recommended by Kolthoff (15): $V = V^0 + (Rt/n\mathbf{F}) \ln (Ox)/(Red)$.

A comparison of (XIV), (XVIII), and (XIX) shows that the Gibbs electrode potential is proportional to the free enthalpy drop of a reduction (or cathodic) half reaction, it will therefore also be proportional to the free enthalpy gain of an oxidation (or anodic) half reaction (16), i.e.,

$$\Delta\zeta = -n\mathbf{F}V \text{ (for reductions)} \quad (XXIIa)$$

$$\Delta\zeta = +n\mathbf{F}V \text{ (for oxidations)} \quad (XXIIb)$$

It is, therefore, thermodynamically permissible to tabulate electrode reactions in either one of two forms, e.g.,

Half-reaction	$\Delta\zeta^0$	E^0	V^0
$Zn = Zn^{++} + 2e^-$	-1.526 v**F**	$+0.763$ v	-0.763 v
$2Cl^- = Cl_2 + 2e^-$	$+2.7188$ v**F**	-1.3594 v	$+1.3594$ v

or, alternately,

Half-reaction	$\Delta\zeta^0$	E^0	V^0
$Zn^{++} + 2e^- = Zn$	$+1.526$ v**F**	-0.763 v	-0.763 v
$Cl_2 + 2e^- = 2Cl^-$	-2.7188 v**F**	$+1.3594$ v	$+1.3594$ v

used) manner by the introduction of one extra-thermodynamic assumption in one of two alternate forms: (*a*) some reasonable assumption can be made regarding the activities of the single ions; a convenient assumption, but not necessarily the only one, is to take the single ion activity as equal to the mean ion activity of the neutral electrolyte of which it is a part; (*b*) some reasonable but arbitrary value can be assigned to the effect of a salt bridge in the interpretation of the measurable potential difference $V'' - V'$ of cells of the type of (XVII*a*), (XVII*b*), or (XVII*c*). Theoretical calculations (12) based on assumption (*a*) show that salt bridges of KCl or NH_4NO_3 introduce an effect not in excess of a few millivolts in the measured potential difference $V'' - V'$. For many purposes in electrochemistry, an effect of this magnitude is entirely negligible and the effect of the salt bridge can then be arbitrarily set equal to zero, or it can be incorporated, as an arbitrary additive constant, in the potential V' of the reference electrode.

[10] See, for example, the equation developed by Gibbs (13) for the potential of the metallic electrode *a* which, with a trivial change in notation, can be written in the form $V'' - V' = (Rt/n_a\mathbf{F}) \ln \gamma_a/G$, where γ_a is the density (presumed small) of the cations *a* in solution and *G* is analogous to Nernst's "metal solution pressure."

In both tabulations, the Gibbs electrode potential V retains the same sign, while the half-cell emf E changes sign, as has been fully discussed above. The whole-cell emf E corresponding to the Lewis and Randall and the Stockholm Commissions' Conventions can be obtained from the Gibbs electrode potential through the relation $E = V_{right} - V_{left}$. The electrode potential of the Stockholm Commissions coincides in every important respect with the Gibbs electrode potential V.

The two most important properties of the Gibbs electrode potential V, (not possessed by the Nernst-Lewis-Latimer half-cell emf E) are (*a*) a sign independent of the direction of current flow, and (*b*) an operational definition in terms of quantities directly observable in the laboratory. These two properties make the Gibbs V the simpler, the more elegant, the more useful by far of the two concepts.

It is the sincere hope of the author that all American chemists will accustom themselves to the use of the Gibbs electrode potential V and thereby rediscover another gem in the scientific heritage of one of our own great masters, of whom it might be said, as it was said of another Master: "A prophet is not without honor, save in his own country, and in his own house" (17).

(*Note added in proof*) The proof given above of the sign invariance of the Gibbs electrode potential V upon a reversal of the half-cell reaction is essentially the same as that already given by S. Barnartt [*This Journal*, **102,** 16*C* (1955)].

REFERENCES

1. J. A. Christiansen and M. Pourbaix, *Compt. rend.* XVII *Conf. inter. union pure and appl. chem.*, held in Stockholm in 1953, pp. 82–84, Maison de la Chimie, Paris (1954).
2. G. N. Lewis and M. Randall, "Thermodynamics and the Free Energy of Chemical Substances," chap. XXIX, McGraw-Hill Book Co., New York (1923).
3. W. Nernst, *Z. physik. Chem.*, **4,** 129 (1889); *Berichte*, **30,** 1547 (1897).
4. *See* reference (2), Chapter XXX.
5. W. M. Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions," 2nd ed., Prentice-Hall, New York (1952).
6. R. Abegg, F. Auerbach, and R. Luther, "Messungen elektromotorischer Krafte galvanischer Ketten," Abhandlungen der deutschen Bunsengesellschaft, No. 5, Halle (1911).
7. *See* J. J. Lingane, "Electroanalytical Chemistry," p. 33, Interscience Publishers, Inc., New York (1953).
8. J. Willard Gibbs, *Trans. Conn. Acad. Arts Sci.*, **3,** 108, 343 (1875–1878); reprinted as pp. 55–349 in "The Collected Works of J. Willard Gibbs, Volume I, Thermodynamics," pp. 331–349, Longmans Green, New York (1928).
9. Michael Faraday, "Experimental Researches in Electricity," p. 113, No. 576 of Everyman's Library, J. M. Dent and Sons, Ltd., London (1914).
10. Th. DeDonder and P. Van Rysselberghe, "Thermodynamic Theory of Affinity," Stanford University Press (1936); P. Van Rysselberghe, *This Journal*, **102,** 43*C* (1955).
11. E. A. Guggenheim, "Thermodynamics, An Advanced Treatment for Chemists and Physicists," chap. IX and X, North Holland Publishing Co., Amsterdam (1949).
12. D. A. MacInnes, "The Principles of Electrochemistry," chap. 13, Reinhold Publishing Co., New York (1939).
13. J. Willard Gibbs, Letter to Professor Wilder D. Bancroft of Cornell University, May, 1899; reprinted in "Collected Works," Vol. I, p. 429.
14. *See* reference (2), chap. XXII.
15. I. M. Kolthoff and E. B. Sandell, "Quantitative Inorganic Analysis," Macmillan Co, New York (1946).
16. A. J. deBethune, *Corrosion*, **9,** 336 (1953); *This Journal*, **101,** 252*C* (1954).
17. Matthew, chap. 13, Verse 57.

THE ELECTROCHEMICAL SOCIETY, INC.

The Electrochemical Society is an international organization of individuals and companies concerned with or interested in Electrochemistry and allied subjects.

The Society is dedicated to the advancement of the theory and practice of Electrochemistry and related subjects, as shown in the following divisions:

Battery	Electro-Organic
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Electric Insulation	Industrial Electrolytic
Electrodeposition	Theoretical Electrochemistry
Electronics	

Among the means to this end are the holding of meetings for the reading and discussion of professional and scientific papers on these subjects, the publication of such papers, discussions, and communications as may seem appropriate, and cooperation with chemical, electrical, and other scientific and technical societies.

It is an incorporated society without capital stock. The affairs of the Society are managed by a Board of Directors under a Constitution and Bylaws. Officers are nominated by a nominating committee appointed by the Board of Directors and elected by the members.

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FUTURE MEETINGS OF
The Electrochemical Society

San Francisco, April 29, 30, May 1, 2, and 3, 1956

Headquarters at the Mark-Hopkins Hotel

Sessions will be scheduled on

**Corrosion (joint symposium with Theoretical),
Electric Insulation, Electronics (including Instrumentation, Luminescence,
Oxide-Cathodes, Phosphor Application, and Semiconductors),
Industrial Electrolytics, Electrothermics and Metallurgy,
and probably Theoretical Electrochemistry**

* * *

Cleveland, September 30, October 1, 2, 3, and 4, 1956

Headquarters at the Statler Hotel

* * *

Washington, D. C., May 12, 13, 14, 15, and 16, 1957

Headquarters at the Statler Hotel

* * *

Buffalo, October 6, 7, 8, 9, and 10, 1957

Headquarters at the Statler Hotel

* * *

New York, April 27, 28, 29, 30, and May 1, 1958

Headquarters at the Statler Hotel

* * *

Ottawa, September 29, 30, October 1, and 2, 1958

Headquarters at the Chateau Leurier

* * *

Papers are now being solicited for the meeting to be held in San Francisco. Triplicate copies of each abstract (*not exceeding 75 words in length*) are due at the Secretary's office, 216 West 102nd Street, New York 25, N. Y., *not later than January 2, 1956* in order to be included in the program. *Please indicate on abstract for which Division's symposium the paper is to be scheduled.* Complete manuscripts should be sent in triplicate to the Managing Editor of the JOURNAL at the same address.

Current Affairs

Hanson-Van Winkle-Munning—ECS Sustaining Member

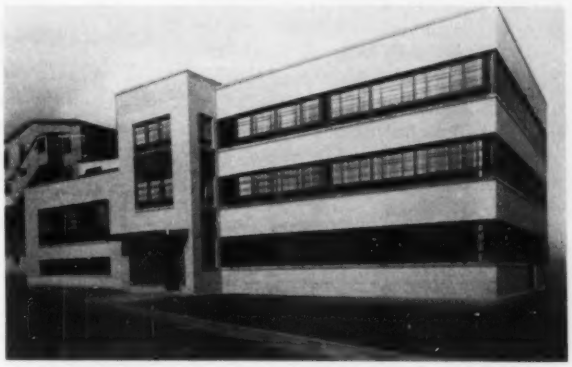
The Hanson-Van Winkle-Munning Co., manufacturers of electroplating and polishing equipment and supplies, is the outgrowth of the merger in 1927 of the A. P. Munning Co., of Matawan, N. J., and the pioneer in the industry, the Hanson and Van Winkle Co. of Newark, N. J. At that time all activities were transferred to Matawan where the main office and manufacturing plant are still located. With the acquisition of the J. C. Miller Co. in Grand Rapids a year ago, the manufacturing activities in the Midwest area were transferred recently from Anderson, Ind., to Grand Rapids. Sales offices, warehouses, and technical service centers are located in the principal manufacturing areas of the United States. Export business is carried on through agents in various parts of the world.

The Hanson and Van Winkle Co. of Newark, N. J., was founded in 1820, when the infant manufacturing industries in this century were dependent upon the Old World for their supplies, and for a period of 50 years it was engaged principally in importing drugs, oils, chemicals, and dye stuffs and also acting as agents for manufacturers of acids and chemicals as their production was established in the United States. In the early 70's, the necessity of engaging in manufacture was forcibly presented to the company by an increase in the number of well-established chemical industries, keen competition, and the consequent falling off of the profits of the agent or middle man.

Although the art of electroplating, one of the greatest inventions in the 19th century, has been stimulated greatly by the discovery of Elkington and Wright of a commercial silver plating process with patents issuing in 1840, it was practiced very little in the United States until 1870. The Hanson and Van Winkle Co. had added to their established business line supplies required by silver platers, such as batteries, battery parts, chlorides of the metals, and several chemicals and materials used for plating and polishing, but it was not until about 1870, when a patent was granted to Dr. Adams for sulfate of nickel and ammonia to be used as an electrolyte for depositing nickel, that their attention was directed to the dawning possibilities of the electroplating industry. Shortly thereafter the Hanson and Van Winkle Co. started in a small way to manufacture cast nickel anodes and nickel ammonium sulfate salts.

The company was now closely identified with the nickel plating industry in its earlier stages and looked about for a wider field. At about this time, Mr. Edward Weston designed a practical dynamo suitable for the electrodeposition of metals. A factory was set up in Washington St., Newark, N. J., and in 1874 the manufacture of the first low voltage dynamo made in the United States was undertaken. This was with the financial aid and encouragement of the Hanson and Van Winkle Co. whose head, Mr. Abraham Van Winkle, was the first President of the Weston Electric Dynamo Co.

The success of this dynamo was immediate and its sale was world wide, the Hanson and Van Winkle Co. receiving the highest award of the United States Centennial Commission at the International Exhibition in Philadelphia in 1876 and later at the American Institute in New York and the Exhibition Universale Internationale in 1878 in Paris.



Exterior view of the new Hanson-Van Winkle-Munning Co. laboratory at Matawan, N. J.

The early electroplating efforts were confined mainly to nickel and silver. The substitute of cheaper sheet steel for the more precious metals created a demand for brass, bronze, copper, and zinc coatings, which was further increased by the introduction of lacquer suitable for protecting the electroplated finish upon chandeliers, builders' hardware, lamps, and ornaments. The Hanson and Van Winkle Co. introduced celluloid lacquer in 1886. Its success was immediate and the assurance that plated articles could be satisfactorily protected gave an added impetus to the demand for electrical equipment. The company then applied itself to the problem of providing mechanical and automatic devices for use in electroplating and it is primarily due to this early effort that the mechanical methods now so widely used were introduced to the trade.

Today, the Hanson-Van Winkle-Munning Co. is one of the foremost concerns manufacturing equipment and supplies for electroplating, anodizing, polishing, and buffing. Some of the principal products are semi- and full-automatic conveyors, continuous strip or wire plating and cleaning equipment, low voltage motor generators, rectifiers and rheostats, plating barrels, polishing wheels, buffs, bar and liquid compounds, anodes, chemicals, electroplating processes, special galvanizing fluxes, and a host of other products used in the metal finishing field.

A modern electrochemical laboratory was erected in 1948 housing research, customers' service, and plant control activities. At present these laboratory facilities are being expanded to provide for a considerable increase of scientific activities.

NEWS ITEMS

1954 Semiconductor Abstracts Available

"Abstracts of the Literature on Semiconducting and Luminescent Materials and Their Applications—1954 Issue" will be available about November 15. With the 1954 issue, two full years of organized abstracts on the solid state electronic device industry can be obtained from John Wiley & Sons, Inc. 440 Fourth Avenue, New York, N. Y. The 1954 Issue, like the 1953, was compiled by Battelle Memorial Institute and sponsored by The Electrochemical Society.

The 1954 format is essentially the same as the 1953 issue, providing even greater detail in each abstract. Over 220 abstracted articles are devoted to germanium, silicon, and their applications. The entire volume contains abstracts of over 750 articles.

To persons concerned with the broad, growing field of semiconducting and luminescent materials and their applications, keeping up with the contributions from so many branches of science in an almost hopeless task since articles appear in so many different periodicals published all over the world. To service these and other interested people, The Electrochemical Society initiated a long-range project last year to publish annually abstracts, prepared by Battelle Memorial Institute, in this field.

Members of the Society who wish to buy the book, listed at $5.00, at the 33⅓% member discount should send their orders to The Electrochemical Society, 216 West 102nd St., New York 25, N. Y. The Society will then forward orders to John Wiley & Sons, Inc., who will ship the volume with the invoice. To receive the member discount, *orders must* be sent to Society Headquarters.

Analysis of Jet-Engine Alloys

The National Bureau of Standards has developed an accurate procedure for analyzing cobalt-base jet-engine alloys through use of ion exchange. The procedure permits the quantitative determination of nickel, manganese, cobalt, and iron in the presence of niobium, molybdenum, tantalum, tungsten, silicon, and copper. Development was carried out by J. L. Hague, E. E Maczkowske, and H. A. Bright of the Bureau's Analytical Chemistry Section.

The NBS procedure was designed particulary for the analysis of an S-816 type of alloy containing 40% cobalt, 20% nickel, 20% chromium, and 4% each of niobium, tungsten, and molybdenum. The remainder of the alloy is largely iron, manganese, carbon, and silicon.

1955 Annual Index

The Annual Index for Volume 102 (1955) of the JOURNAL will appear in the February 1956 issue rather than in the December 1955 issue.

Nominations for 1956 Acheson Award

William Blum, Chairman of the Acheson Medal Award Committee, would like to receive suggestions for possible candidates for the next Acheson Medal Award, to be made in the fall of 1956.

The procedure to be followed by the membership, taken from the Rules Governing the Award of the Acheson Medal, is given below.

1. Nominations shall be accepted from the membership at large.

2. All nominations, whether made by a member of the Nominating Committee or by any other member of the Society, must be accompanied by a full record of qualifications of the nominee for the award. Such supporting documents from friends of the candidate or from his organization shall be in order.

3. The nominator must assume the responsibility for providing the Chairman of the Nominating Committee with nine copies of the supporting documents, one for each member.

Nominations must be sent to the Chairman not later than March 1 of the year in which the medal is awarded and nominations will be considered closed after that date.

All nominations of candidates for the medal shall be continued in force for a period of two consecutive awards of the medal. Any unsuccessful candidate may be renominated in the usual manner for any subsequent Medal award.

Correspondence should be addressed to William Blum, 2311 Connecticut Ave. N.W., Washington 8, D. C.

Aluminum Centenary

The India Section of The Electrochemical Society, the Indian Institute of Metals (Bangalore Chapter), the Association of Scientific Workers of India (Bangalore Branch), and the Scientific Film Society celebrated the Aluminum Centenary on September 19 and 21 at the Indian Institute of Science, Bangalore. Professor M. S. Thacker, Chairman of the India Section, inaugurated the function and Professor Brahm Prakash, Head of the Department of Metallurgy, Indian Institute of Science, presided.

The following papers were presented: (*a*) "A Perspective of the Indian Aluminum Industry" by Mahesh Chandra, Indian Aluminium Co.; (*b*) "Some Aspects of Aluminum Research in India" by E. G. Ramachandran, Indian Institute of Science; (*c*) "Aluminum in Consumer Industries in India" by N. R. Srinivasan; (*d*) "Aluminum in Telecommunication Industry" by S. Krishnamurthy, Indian Telephone Industries.

There was an interesting discussion, and the program was rounded off with technical films on aluminum.

T. L. RAMA CHAR, *Regional Editor, India*

The Practical Utilization of Recorded Knowledge—Present and Future

A Conference on The Practical Utilization of Recorded Knowledge—Present and Future will be held at Western Reserve University, Cleveland, Ohio, January 16–18, 1956, for business, government, research management, scientists, lawyers, doctors, librarians, information specialists, educators, equipment manufacturers, and others concerned with the effective management of recorded information, offered by The School of Library Science and its Center for Documentation and Communication Research, Western Reserve University.

Working committees representing more than 50 industrial, educational, institutional, and governmental organizations are preparing seven "state-of-the-art" papers for distribution before the conference to registered delegates. These papers, which will form the basis for the conference deliberations, will be concerned with: (*a*) defining the characteristics of recorded information; (*b*) describing the research and decision-making processes; (*c*) identifying the ways and means in which research workers, executives, and others use information; (*d*) inventorying and providing a basis for evaluation of existing systems for analysis, storage, and retrieval of information; (*e*) developing a system of documentation terminology that can

be used at the conference; (*f*) surveying the various fields concerned with information organization and identifying "contact points" for the ultimate organization of cooperative programs; (*g*) surveying and summarizing the present status of education programs for the training of librarians, documentalists, and information specialists.

In order that these "state-of-the-art" papers may be distributed well in advance of the conference for study by the delegates, registration should be made as soon as possible. The registration fee is $10; checks should be made payable to Western Reserve University and sent to Dean Jesse H. Shera, School of Library Science, Western Reserve University, Cleveland 6, Ohio.

NACE Meeting to Stress Reduction of Corrosion Losses

Means of reducing the nation's multibillion dollar annual loss due to corrosion will be stressed at the 12th Annual Corrosion Conference of the National Association of Corrosion Engineers, March 12–16, 1956, at the Hotel Statler, New York City. Persons from all parts of the world have been invited to participate in discussions and information exchanges on many aspects of corrosion control.

A variety of discussions devoted to corrosion principles, chemical inhibitors, corrosion problems in the petroleum industry, oil and gas production, chemical industry, steel metallurgy, power and communications, pipeline problems, corrosion by high purity water, cathodic protection, high temperature corrosion, plastics, protective coatings, and instrumentation will be featured. In addition, three educational lectures will be given on: Mechanism of Corrosion Inhibitor Action, Relationship of Thin Films to Corrosion and Techniques of Thin Film Study, and Effects of Velocity on Corrosion.

The 1956 Corrosion Show will be held concurrently with the conference. It will feature exhibits of the latest equipment and techniques for control and prevention of corrosion. Companies throughout the world engaged in the fight against corrosion have been invited to exhibit at the show.

7th Annual Dinner of Chemical Profession in Cleveland

The Seventh Annual Dinner of the Chemical Profession in Cleveland was held in the Hotel Hollenden, Cleveland, on Thursday, October 27, at 7:00 P.M. Dr. Henry Eyring, Dean of the Graduate School of the University of Utah, spoke on "Inflammation and Stress." Dr. William von Fischer, head of the Department of Chemistry of Case Institute of Technology, was toastmaster. The Third Annual Awards were presented for services in promoting the chemical profession in the Cleveland area. The dinner is sponsored by the Cleveland Sections of the American Chemical Society, The Electrochemical Society, the American Institute of Chemists, the American Institute of Chemical Engineers, and Alpha Chi Sigma, the national professional chemists fraternity.

4-Yr. Anode Performance Report

A report on the performance of anodes for impressed currents tested for four years in soils has been completed and is scheduled for publication. The report, "Final Report on Four Anode Inspections at Ground Beds Installed by Mississippi Power and Light Company for Committee Test Program," is by Technical Unit Committee T-2B on Anodes for Impressed Currents, one of the group in the pipeline field for the National Association of Corrosion Engineers, Houston, Texas.

Carbon, graphite, and steel anodes were tested in natural soils and carbonaceous backfill. Details concerning ground bed construction were included in NACE Publication 50-1. Positive results were obtained in the tests, and variations in performance are great enough to permit deductions concerning anode performance under similar conditions of installation.

The report also includes recommendations on anode type, ground bed sites, backfill, and installation methods. Tables show anode current and net anode resistance for the four-year test period.

Ceramics for Piezoelectric Transducers

The National Bureau of Standards has developed several lead-oxide based piezoelectric ceramics that have excellent electromechanical properties and are stable over a wide temperature range. Some of these compositions, particularly in the lead titanate–lead zirconate system and the lead titanate–lead zirconate–lead oxide: tin oxide system, are expected to find considerable application as transducers for sensing elements in accelerometers, sound detectors, sonar, velocimeters, strain and pressure gauges, and as drivers in ultrasonic devices. These materials can be expected to replace barium titanate in many commercial applications and to extend the use of ceramic transducers. The compositions were developed by

MANUSCRIPTS AND ABSTRACTS FOR SPRING MEETING

Papers are now being solicited for the Spring Meeting of the Society, to be held at the Mark-Hopkins Hotel in San Francisco, April 29 and 30, and May 1, 2, and 3, 1956. Subjects to be covered at the technical sessions will be Corrosion (joint symposium with Theoretical) Electric Insulation, Electronics (including Luminescence, Oxide-Cathodes, Phosphor Application, Semiconductors, and Instrumentation), Industrial Electrolytics, Electrothermics and Metallurgy, and Theoretical Electrochemistry.

To be considered for this meeting, triplicate copies of abstracts (not to exceed 75 words in length) must be received at Society Headquarters, 216 West 102nd St., New York 25, N. Y., *not later than January 2, 1956. Please indicate on abstract for which Division's symposium the paper is to be scheduled.* Complete manuscripts should be sent in triplicate to the Managing Editor of the JOURNAL at the same address.

***

The Fall 1956 Meeting will be held in Cleveland, Ohio, September 30, October 1, 2, 3, and 4, at the Statler Hotel. Sessions will be announced in a later issue.

B. Jaffe, R. S. Roth, and S. Marzullo of the Bureau's mineral products laboratories under the sponsorship of the Army's Office of Ordnance Research.

ACS Spring 1956 Meeting

At the spring (April) 1956 national meeting of the American Chemical Society in Dallas, Texas, there will be a Symposium on Thermogravimetry and Differential Thermal Analysis, jointly sponsored by the Division of Analytical Chemistry and the Division of Physical and Inorganic Chemistry. Topics to be included are the applications of these techniques to investigations of reaction mechanisms, kinetic studies, the determination of physicochemical and thermodynamic properties of inorganic and organic systems, as well as their analysis both qualitative and quantitative.

Papers will be considered for presentation at this symposium if prospective authors will submit two copies of a 200-word abstract and a 1000-word abstract, or the manuscript, *by December 15, 1955*, to the chairman, Dr. Saul Gordon, Pyrotechnics Chemical Research Lab., Picatinny Arsenal, Dover, N. J. Regulations of the American Chemical Society require that: "No paper by a chemist or chemical engineer *residing* in the United States who is not a *member* of the society shall appear on the program of a national, regional, divisional, or other major meeting of the society unless it be a joint paper with one or more society *members*."

Elemental Boron

The Pacific Coast Borax Co., Division of Borax Consolidated, Ltd., New York City, after 2½ years of research work, has started the manufacture of elemental boron on a pilot plant scale. From the beginning of the research program the production of boron of 89 to 90% purity offered no difficulty. Their aim—amorphous boron of much higher quality at a price for commercial quantities which would remove it from the class of laboratory curiosities to that of an industrial chemical—has been achieved. Two grades of amorphous boron, a low grade of 90 to 92% and a high grade of 95 to 97%, are to be offered in the price range of $10 to $13 per lb and $12 to $15 per lb, respectively, in volume quantities of 2000 lb or more. Sample and test quantities are being offered at somewhat higher prices.

Lion Oil, Monsanto Chemical Merger

The merger of Lion Oil Co. into Monsanto Chemical Co., as agreed upon by the directors of both corporatons and approved by Monsanto and Lion shareowners, became effective on September 30.

Lion Oil Co. is now a division of Monsanto. T. M. Martin, who was President of Lion Oil Co., is serving as President of the Lion division, and, in addition, has been elected a vice-president of Monsanto by the Monsanto board.

American Leadership in Science and Engineering

American leadership in science and engineering, not only on defense projects but throughout our economy, is the most powerful deterrent to international aggression, Don G. Mitchell, Chairman and President of Sylvania Electric Products Inc., declared on September 15 at the dedication of the company's new Waltham Laboratories, which are engaged in highly advanced projects relating to guided missiles and aviation electronics. Mr. Mitchell stressed the joint role of the Armed Services and industry in national security.

Also speaking on the dedication program, Lt. Gov. Sumner G. Whittier of Massachusetts described the vital importance of the electronics industry to the continued progress of the Commonwealth and New England, and Dr. Carl S. Ell, President of Northeastern University, cited the responsibilities of the nation's colleges and universities in assuring technical leadership. Dr. O. G. Haywood, manager of the Waltham Laboratories, presided at the ceremonies which were attended by several hundred representatives of the Armed Services, commerce and industry, education, government, and the press.

National Research Exhibit at Atomic Trade Fair

National Research Corp., Cambridge, Mass., was among more than 70 American industrial exhibitors, in addition to U. S. and foreign governmental organizations and research contractors, participating in the first U. S. Trade Fair of the Atomic Industry, held at the Sheraton-Park Hotel in Washington, D. C., Sept. 27–30, in conjunction with the Annual Fall Meeting of the Atomic Industrial Forum.

National Research Corp.'s exhibit featured projected slides showing the company's research and manufacturing operations of interest to the peacetime atomic energy industry. An exhibit booth displayed NARESCO high vacuum equipment and titanium castings prepared by a new National Research process.

First Film on Ductile Cast Iron

The first motion picture film on the properties and applications of ductile cast iron has been released by The International Nickel Co., Inc., 67 Wall St., New York, N. Y., and is now available for use by industry, technical societies, and educational institutions.

The 15-min sound, color film, "Ductile Cast Iron," graphically illustrates the fact that the new engineering material which can be cast like gray iron has properties similar to steel. The ductility of the iron is illustrated by bending, twisting, impact, and tensile tests. It incorporates five years of pro-

JUNE 1956 DISCUSSION SECTION

A Discussion Section, covering papers published in the July–December 1955 JOURNALS, is scheduled for publication in the June 1956 issue. Any discussion which did not reach the Editor in time for inclusion in the December 1955 Discussion Section will be included in the June 1956 issue. Those who plan to contribute remarks for this Discussion Section should submit their comments or questions in triplicate to the Managing Editor of the JOURNAL, 216 W. 102nd St., New York 25, N. Y., *not later than March 1, 1956*. All discussions will be forwarded to the author, or authors, for reply before being printed in the JOURNAL.

duction experience and use of the material. Among the illustrated applications are gears, pinions, plow shares, pistons, and pneumatic couplings. Uses of ductile cast iron are also shown for a variety of industries.

Rolling Fuel Elements

Four 2-high/4-high Combination Rolling Mills being built by Stanat Manufacturing Co., Inc., Long Island City, N. Y., for installation at the Atomic Energy Commission's Argonne National Lab., Lemont, Ill. Chosen for their versatility, ruggedness, and precision, these machines are being especially adapted for use in conjunction with hoods and remote control handling equipment to facilitate rolling of pyrophoric materials. Scheduled to begin operation early in 1956, the mills will constitute a major tool in the processing of the plutonium-containing fuel elements which are so essential to the development and operation of fast breeder reactor power plants.

Bucknell's New Olin Science Bldg.

Dr. John C. Warner, President of the Carnegie Institute of Technology, spoke at the dedication on September 28 of Bucknell University's new F. W. Olin Science Building, gift of the Olin Foundation. In his address, he expressed the conviction that use of the scientific method, in modified form, could help solve many of our current social, political, and economic problems.

Formal presentation of the building to the university by Dr. Charles L. Horn, President of the Foundation, highlighted the ceremony attended by more than 2000 students, teachers, and invited guests. Dr. William H. Coleman, Vice-President and Dean of the college, accepted the building which contains a memorial plaque dedicating the structure "to the advancement of science and to the preparation of youth for service in the world of tomorrow." The honorary degree of doctor of science was conferred upon Dr. Warner and four other noted scientists by President Merle M. Odgers.

Nuclear Engineering and Science Congress

The first full-scale look at atomic energy in industry, government, education, medicine, and agriculture by the nation will take place at the Nuclear Engineering and Science Congress and the Atomic Exposition to be held in Cleveland, Ohio, December 12–16, 1955.

The Congress, coordinated by the Engineers Joint Council, represents the biggest single project ever undertaken by the combined engineering and scientific societies of the nation, more than 25 of whom are cooperating in the effort. Nearly 300 papers describing the latest developments in nuclear engineering and science will be presented in technical sessions to the more than 2000 persons expected to attend. In addition to the societies, the Congress is actively supported by private enterprise and the government.

Running concurrently with the Congress and supplementing its discussions of nuclear developments will be an Atomic Exposition to display the current actual tools of atomic developments—reactors, components, equipment, materials, and services in the atomic power field. This Exposition will include many initial displays of nuclear equipment and will be open to the public on December 10 and 11.

Industrial Productivity Forum

In an illustrated talk at the Salt Lake City Industrial Productivity Forum at the Hotel Newhouse, September 19, Norman F. Barnes of the G. E. General Engineering Lab., Schenectady, N. Y., presented figures strongly emphasizing that research and development are becoming the lifeblood of industrial existence. He stated that, since 1950, expenditures in development programs have been equal to the combined total of all the years since the so-called industrial revolution and that, in the next ten years, American industry is expected to spend more than three times the total for the past five years on research and development.

The Forum was presented by the Utah Power and Light Co. and the General Electric Co.

DIVISION NEWS

San Francisco Meeting Abstract Deadline

Abstracts, *not to exceed 75 words in* length, of papers to be scheduled for presentation at the San Francisco Meeting of the Society must be received at Society Headquarters, 216 W. 102nd St., New York 25, N. Y., *not later than January 2, 1956. Please indicate on the abstract for which Division's symposium the paper is to be scheduled.*

There will be technical sessions on: Electric Insulation, Electronics (including Instrumentation, Luminescence, Oxide-Cathodes, Phosphor Application, and Semiconductors), Industrial Electrolytics, Electrothermics and Metallurgy, and Theoretical Electrochemistry.

Three special symposia are planned: (*a*) semiconducting materials, surface controlled phenomena, and chemical process technology, sponsored by the Semiconductor Group of the Electronics Division; (*b*) "Rare Earths" and "Electric Arcs in Inert Atmospheres and Vacuum," sponsored by the Electrothermics and Metallurgy Division; (*c*) "Adsorption Phenomena at Electrode Surfaces," sponsored by the Theoretical Electrochemistry and Corrosion Divisions.

E & M Rare Earth Symposium, May 1956

The Electrothermics and Metallurgy Division is soliciting papers for the April 29–May 3, 1956 Society Meeting in San Francisco. The subject of one symposium will be "Rare Earths." Original papers are requested rather than reviews of previously reported studies. Also, a number of papers in the general field of chemical metallurgy are desired.

Authors who wish to present papers should submit a *75-word abstract* to W. H. Smith, General Electric Research Laboratory, P. O. Box 1088, Schenectady, N. Y., *not later than January 2, 1956.*

E & M Symposium on "Electric Arcs in Inert Atmospheres and Vacuum"

The Electrothermics and Metallurgy Division is planning a symposium on the general subject of "Electric Arcs in Inert Atmospheres and Vacuum" to be held in San Francisco, April 29–May 3, 1956.

Papers representing new or original work rather than revisions or repetitions of previously published information are now being solicited.

It is planned to present a program that provides a thorough but balanced treatment of the general subject of inert and vacuum arcs. Early plans are to divide the sessions as follows:

1. One half-day session on experimental and theoretical studies of high current arcs in inert gases (pressure or vacuum) and vacuum. Papers may include such topics as magnetic effects; effect of frequency on a-c arcs; characteristics of arcs using different metal electrodes or different gases;

energy distribution in arcs; heat transfer mechanism, etc.

2. Two half-day sessions on the application of electric arcs in inert gases and vacuum to the design and operation of arc furnaces. Suggested subjects under this heading are: descriptions of consumable and nonconsumable electrode furnace designs; systems and methods of arc control; power supplies; operation of arc furnaces with respect to materials handling problems, safety considerations, cost of melting, etc.; design of production furnaces and experimental furnaces; design and operation of arc casting furnaces; fabrication of electrodes for consumable arc melting furnaces; problems of homogeneity, etc.

3. One half-day session to be devoted to the "cold crucible" arc melting of individual metals. Both the highly reactive metals such as titanium, zirconium, tantalum, niobium, etc., and the more common metals and alloys such as iron, nickel, steel, and alloy steels are to be considered. Suggested subjects are: advantages and disadvantages of the cold crucible process compared with other melting techniques; comparisons of the mechanical and physical properties of metals arc melted in inert atmospheres or vacuum, etc.

4. One half-day session to include papers on reactions in inert and vacuum arcs (pressure arcs included). Subjects welcomed under this heading are: reduction reactions in arcs; production of pure compounds and intermetallics; degassing reactions; thermodynamics of reactions in high temperature arcs, etc.

It is also hoped to include in this session papers on applications of inert and vacuum arcs other than the melting applications.

Authors who wish to present papers should (1) notify the undersigned of his interest and submit title of proposed paper as early as possible for planning purposes, (2) submit a 75-word abstract not later than January 2, 1956.

WILLIAM E. KUHN
(1956 Chairman)

Mailing Address:
The Carborundum Company
Research and Development Division
Niagara Falls, N. Y.

Symposium on Adsorption Phenomena at Electrode Surfaces

The Theoretical Electrochemistry and Corrosion Divisions are planning a symposium on "Adsorption Phenomena at Electrode Surfaces" for the Spring Meeting of the Society in San Francisco, April 29 to May 3, 1956. The symposium will extend to all types of electrode processes in which adsorption phenomena are involved. Special emphasis will be placed on adsorption phenomena in relation to corrosion and electrode kinetics.

The symposium will consist of both invited papers and contributed papers. *Seventy-five word abstracts* of all contributed papers should be sent in triplicate to The Electrochemical Society, 216 W. 102nd St., New York 25, N. Y., *on or before January 2, 1956.*

The Theoretical Electrochemistry Division also has scheduled the following symposia for future meetings:

1. Fundamental Aspects of Electrodeposition—Joint Symposium with Electrodeposition Division, October 1956, Cleveland.

2. Electrolytes—Spring 1957, Washington, D. C.

3. Electrokinetic Phenomena—Fall 1957, Texas.

Extensive plans already are being made for the symposium on electrolytes which is expected to involve the structure and general properties of both aqueous and nonaqueous systems, including fused salts.

NEW MEMBERS

In October 1955 the following were approved for membership in The Electrochemical Society by the Admissions Committee:

Active Members

DONALD G. CARLTON, Washington Steel Products, Inc., 1940 E. 11th, Tacoma, Wash. (Electrodeposition, Theoretical Electrochemistry)

ANTONIO A. DA SILVA, A. A. Silva; Mail add: Avenida 24 de Julho, 26-B, Lisbon, Portugal (Battery)

NOLAN DOUGLAS MARCHAND, The Dow Chemical Co.; Mail add: 1613 W. Second St., Freeport, Texas (Industrial Electrolytic)

ALLAN E. MARTIN, Vanadium Corp. of America, Research Center, Cambridge, Ohio (Electrothermics & Metallurgy)

WALTER J. MOORE, Chemistry Dept., Indiana University, Bloomington, Ind. (Corrosion, Electronics, Theoretical Electrochemistry)

HOWARD ROSENTHAL, RCA Labs., Princeton, N. J. (Electronics)

JOHN L. SIENCZYK, Arthur D. Little, Inc.; Mail add: 9 Medford St., Chelsea 50, Mass. (Electrodeposition, Industrial Electrolytic)

RICHARD SPRINGER, Consulting Chemist; Mail add: 84 Menselssohnstr., Frankfurt/Main, Germany (Corrosion, Electrodeposition)

Student Associate Member

ANDRÉ T. MORKEL, Corrosion Lab., Massachusetts Institute of Technology, Cambridge 39, Mass. (Corrosion)

PERSONALS

J. BALACHANDRA, who is in the U. S. A. under the TCM program, is now at the National Bureau of Standards, Washington, D. C.

T. L. RAMA CHAR has returned to Bangalore after completion of his visit to the U. S. A. under the TCM program.

S. SOUNDARARAJAN has been awarded the Ph.D. degree by the University of Madras.

JOHN B. MERRILL

John B. Merrill and his wife, the former Ann Tompkins, of Towanda, Pa., were killed in the United Air Lines crash near Laramie, Wyo., on October 6. Mr. Merrill was 45 years of age.

Mr. Merrill was a Vice-President–Operations in charge of the Tungsten and Chemical, Atomic Energy, Electronics, and Parts divisions of Sylvania Electric Products Inc. He joined the Sylvania organization in 1941 in Towanda, Pa., as Superintendent of the fluorescent powder operation, purchased at that time from the Patterson Screen Co. Upon completion of the new plant in Towanda in 1943, Mr. Merrill became Plant Manager, and in 1945 he was appointed General Manager of the newly created Tungsten and Chemical Division. He subsequently was elected a Vice-President and was appointed a Vice-President–Operations in 1953.

A native of Cumberland Center, Maine, Mr. Merrill graduated from Bowdoin College in 1933 and obtained the degree of master of science in physics at Massachusetts Institute of Technology in 1936. For a time he was engaged at M.I.T. in special research work on crystals before joining the Patterson Screen Co. in 1936 as a research physicist. He was superintendent of Patterson's fluorescent powder plant

when Sylvania purchased that operation.

In addition to The Electrochemical Society which he joined in 1946, he was a member of the American Physical Society, the Optical Society of America, and the American Association for the Advancement of Science.

Mr. and Mrs. Merrill are survived by two young children, Peter Gray and Martha Cutter. Mr. Merrill is survived by his mother, Mrs. Wallace L. Merrill, of Cumberland Center, Maine, and a brother, Paul Merrill, of Portland, Maine. Mrs. Merrill is survived by her parents, Mr. and Mrs. Theodore Tompkins, of Towanda.

JOHN PUTMAN MARBLE

John Putnam Marble, Washington, D. C., died in June 1955 at the age of 58.

Dr. Marble was born in Worcester, Mass., on May 30, 1897. He attended Williams College, Williamstown, Mass., graduating with a B.A. degree in 1918. From September 1918 until January 1919 he served as a private in the Chemical Warfare Service, U. S. Army, Research and Control Laboratory, Edgewood Arsenal. He was a part-time special student in physics, chemistry, and mathematics at Clark University, Worcester, Mass., from January to June 1919, and from 1919 until 1926 was engaged in a family dry salt business. He entered Harvard University graduate school in 1926, receiving his M.A. degree in chemistry in 1928 and his Ph.D. degree in analytical chemistry under G. P. Baxter in 1932. He went to Washington in 1931 to do research on analysis of radioactive minerals under the auspices of the National Research Council, continuing work summers on chemical atomic weights at Harvard through 1942. He worked at Yale in the spring of 1939 on the preliminary preparation of thorium standards. At the time of his death he was Chairman of the Committee on Measurement of Geologic Time, Division of Geology and Geography, National Research Council, and an Associate in Mineralogy, U. S. National Museum.

Dr. Marble was the author of some 15 papers on chemical atomic weights of radiogenic leads, analysis of radioactive minerals, analysis of scandium minerals, topics related to measurement of geologic time by absolute methods, portions of reports of National Research Council Committee on Measurement of Geologic Time since 1931.

He was a member of several scientific organizations, including The Electrochemical Society which he joined in June 1918.

BOOK REVIEWS

APPLIED X-RAYS, 4th Edition, by George L. Clark. Published by McGraw-Hill Book Co., Inc., 330 W. 42nd St., New York, N. Y., 1955. ix + 843 pages, $12.50.

The steady burgeoning of the science of x-ray analysis during the past three decades is strikingly reflected in the concomitant growth of this well-known and popular monograph on the subject. The following table gives a picture of the course the development of this book has taken.

	1st Ed. (1927)	2nd Ed. (1932)	3rd Ed. (1940)	4th Ed. (1955)
Total pages	251	470	674	843
General principles	40	59	64	128
Equipment and technique	16	37	77	74
Radiography and radiation effects	28	63	79	136
Crystallography	73	165	235	280
Chemical analysis	3	9	8	14
Size, shape, orientation, strain, polymers, etc.	76	115	200	180

This work attempts to present a comprehensive survey of all of the applications of x-radiation in all branches of scientific work (other than medical therapy). As the author states, "the subject in its manifold phases has grown to such size and to such countless ramifications that it challenges the capacity of any one writer, however experienced, to deal authoritatively with all [of it]." Professor Clark has met this challenge admirably well, and has been quite successful in producing a well-balanced, integrated review of the entire field. The organization of the text is similar to that of the previous (third) edition, differences consisting chiefly in the up-dating and expansion of the exposition of applications, and the description of research achievements.

The work is divided into two major parts: the first concerned with general principles (physics and applications of x-radiations), the second with experimental results (crystal analysis, silicates, alloys, organic structures, glasses, amorphous materials, polymers). The treatment is carefully organized and logically presented, and there is very little that will not be clear to the reader with a reasonably good grounding in

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basic physical chemistry. Unfortunately the book is marred by the presence of a number of typographical errors.

S. Z. LEWIN

ELEKTROLYTISCHE ABSCHEIDUNG UND ELEKTROKRISTALLISATION VON METALLEN by Hellmuth Fischer. Vol. 12 in the series "Reine und angewandte Metallkunde in Einzeldarstellungen." Published by Springer-Verlag, Berlin-Göttingen-Heidelberg, Germany, 1954. xii + 717 pages, 27 illustrations. Price: DM 72 (about $18.00).

This is a comprehensive and modern treatment of the theories of electrode processes with especial attention to cathodic metal deposition. The treatment is somewhat colored by the author's own viewpoints, but the literature is reviewed thoroughly and reference is made to the work of some 500 authors and their co-workers, covering the year 1953. Most of the routine references naturally are to German sources, but important work from other countries is not overlooked. The book should be extremely useful to those who must know, or wish to know, basic principles and theory as well as what is going on in current research. As the author says in the Preface, this field "ist ein Grenzgebiet par excellence. Not only electrochemistry, metal science, crystal physics, and surface chemistry are involved, but frequently chemical kinetics, thermodynamics, colloid chemistry, hydrodynamics, and other matters as well."

Section 1, Electrochemistry, 320 pp., is not a general textbook of the subject, but deals mainly with surface electrochemistry: single and mixed potentials, polarization and overpotential, electrical double layer, depletion and concentration polarization in cathode films, with 200 pp. on mechanism of cathodic deposition. The "modern European" method of treating potentials and thermodynamics is perhaps not very popular in this country.

Section 2, Electrocrystallization, 220 pp., treats theories of crystal nucleation and growth, growth forms, nonmetal codeposition. Section 3, 60 pp., is concerned with such properties of metal deposits as luster, hardness, internal stresses, electrical resistance, adherence, corrosion properties, etc. Section 4, 40 pp., deals with the conditions for deposition and properties of the deposits of some 15 individual metals.

For easy reference the book is divided into rather small numbered sections and has a 6-p. Table of Contents; about 60 pp. are devoted to the Index. The material is well organized and well written. An English translation would be most useful and it is quite possible that one will be published in the near future.

CECIL V. KING

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Expanding research program requires an experienced electrochemist for research and development work on fused salt electrolysis. Salary commensurate with experience.

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American Potash & Chemical Corporation, 201 West Whittier Blvd., Whittier, California.

New Sustaining Member

National Lead Company, Doehler-Jarvis Division, Grand Rapids, Mich., recently became a Sustaining Member of the Society.

Faraday Disc. No. 5 Wanted

Will anyone who has a copy he no longer needs of the *Discussions of The Faraday Society*, No. 5, entitled "Crystal Growth," please contact: Mrs. J. M. Fertig, Research Library, Westinghouse Research Labs., Beulah Rd., Churchill Borough, Pittsburgh 35, Pa.

Volumes Wanted

Will anyone who has a copy he no longer needs of Vol. 86 (1944) and 92 (1947) of the TRANSACTIONS please contact Toshio Keta, 4307 Sheridan St., University Park, Hyattsville, Md.

EMPLOYMENT SITUATIONS

Please address replies to box shown, c/o The Electrochemical Society, Inc., 216 W. 102nd St., New York 25, N. Y.

Positions Wanted

CHEMIST, 36, 11 years' experience, including batteries, electroplating, general physical and chemical commerical testing, seeks New Jersey, Philadelphia, New York City position. *Reply to Box 357.*

CHEMICAL ENGINEER, 40, B.S. degree, 14 years' experience, including materials engineering and research, electrodeposition processes, product engineering and development work involving capacitors. *Reply to Box 358.*

Positions Available

ENGINEERS, ELECTRONIC SCIENTISTS, METALLURGISTS, PHYSICISTS, PHYSIOLOGISTS, PSYCHOLOGISTS, TECHNOLOGISTS. The Naval Air Material Center, located at the Naval Base, Philadelphia, Pa., has vacancies in the above engineering and scientific positions which must be filled. The Center is engaged in an extensive program of aeronautical research, development, experimentation, and test operations for the advancement of Naval Aviation. Engineering vacancies exist in the following options: Electrical, Electronics, General, Industrial, Mechanical, Structural, and Aeronautical (various suboptions). Starting salaries range from $3670 to $8990 per annum. Application for Federal Employment, Standard Form 57, should be filed with the Industrial Relations Dept., Naval Air Material Center, Naval Base, Philadelphia 12, Pa. Applications may be obtained from the above address or information as to where they are available may be obtained from any first or second class post office.

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Notice to Members

By now you have received your official voting ballot from Society Headquarters. If you have not already done so, please return the ballot by *December 15* so that your vote may be included in the final election count.

The Electrochemical Society

INSTRUCTIONS TO AUTHORS OF PAPERS

Address all correspondence to the Editor, JOURNAL OF THE ELECTROCHEMICAL SOCIETY, 216 W. 102nd St., New York 25, N. Y.

FORM

Manuscripts submitted for publication should be in triplicate to expedite review. They should be typewritten, double-spaced, with 2½–4 cm (1–1½ in.) margins.

Title should be brief, followed by the author's name and his business or university connection.

Abstract of about 100 words should state the scope of the paper and give a brief summary of results.

ILLUSTRATIONS

Drawings will be reduced to column width, 8 cm (3⅛ in.), and after reduction should have lettering at least 0.15 cm (1/16 in.) high. Original drawings in India ink on tracing cloth or white paper are preferred. Curves may be drawn on coordinate paper only if the paper is ruled in blue. All lettering must be of lettering-guide quality. See sample drawing on reverse page.

Photographs must be glossy prints and mounted flat.

Captions for all figures must be included on a separate sheet. Captions and figure numbers should not appear in the body of the figure.

General—Figures should be used only when necessary. Omit drawings or photographs of familiar equipment. Figures from other publications are to be used only when the publication is not readily available, and should always be accompanied with written permission for reprinting.

REFERENCES

Literature and patent references should be listed at the end of the paper on a separate sheet, in the order in which they are cited. They should be given in the style adopted by *Chemical Abstracts*. For example:

R. Freas, *Trans. Electrochem. Soc.*, **40,** 109 (1921).

H. T. S. Britton, "Hydrogen Ions," Vol. **1,** p. 309, D. Van Nostrand Co., New York (1943).

H. F. Weiss (To Wood Conversion Co.), U. S. Pat. 1,695,445, Dec. 18, 1928.

UNITS OF MEASUREMENT

Metric units should be used throughout but, where desirable, English units may be given in parentheses.

Corrosion rates in the metric system should preferably be expressed as milligrams per square decimeter per day (mdd), and in the English system as inches penetration per year (ipy).

As regards algebraic signs of potentials, the standard electrode potential for $Zn \rightarrow Zn^{++} + 2e$ is negative; for $Cu \rightarrow Cu^{++} + 2e$, positive.

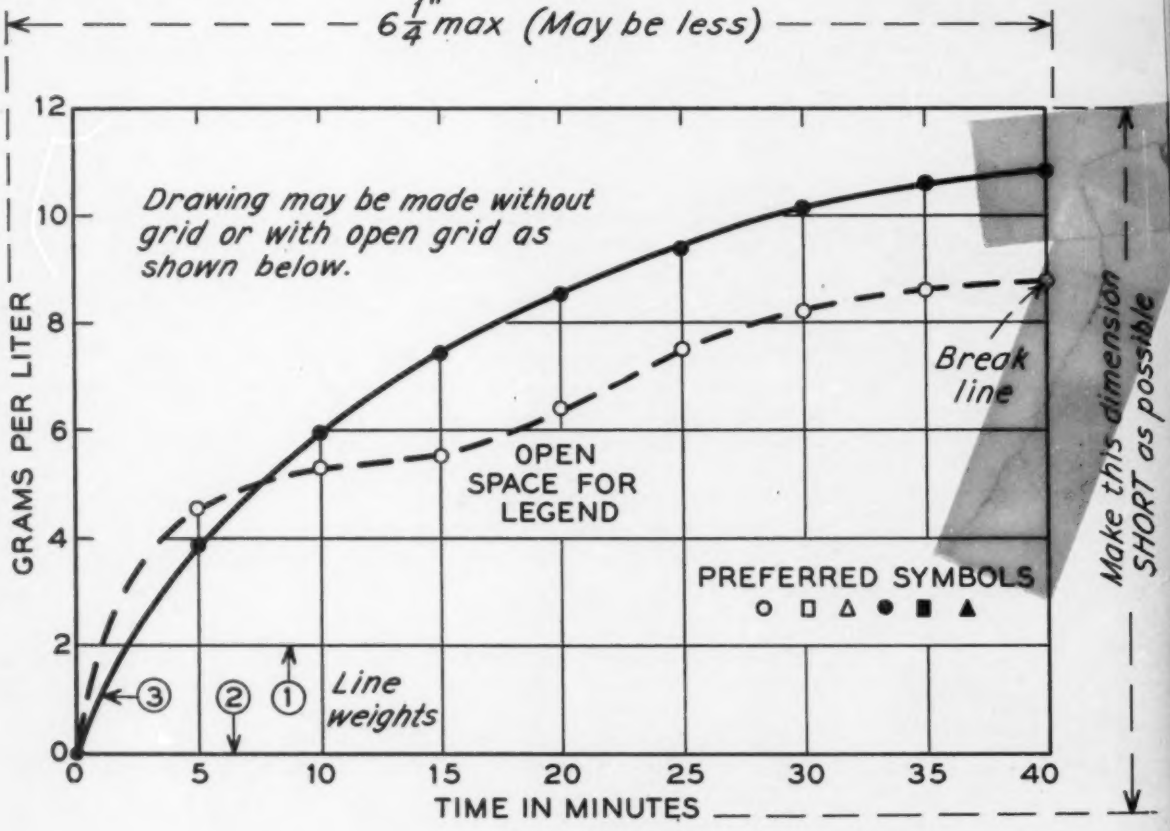
ABBREVIATIONS

Abbreviations should conform with the American Standards Association's li of "Abbreviations for Scientific and Engineering Terms."

GENERAL

Authors should be as brief as is consistent with clarity, and must omit all ma terial which can be regarded as familiar to specialists in the particular field.

The use of proprietary names, trade-marks, and trade names should be avoide if possible. If used, these should be capitalized so that the owner's legal rights ar not jeopardized.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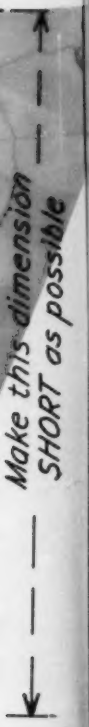

The Effect of Alloying Elements in Iron on Hydrogen Overvoltage and Corrosion Rate in Acid Environments[1]

MILTON STERN[2]

Corrosion Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts

ABSTRACT

Alloying elements commonly found in steel were added to pure iron to establish their effect on hydrogen overvoltage and corrosion rate in 0.1*M* citric acid (*p*H 2.06), 0.1*M* malic acid (*p*H 2.24), and 4% sodium chloride at *p*H 1 and 2. Sulfur, phosphorus, and carbon proved detrimental to corrosion resistance. Copper and manganese were effective in decreasing the detrimental influence of sulfur. Hydrogen overvoltage data are used to explain the particular influences found for various addition elements.

INTRODUCTION

In a previous paper (1) the electrochemical behavior of pure iron in various oxygen-free acid environments was reported. In this investigation, small amounts of various elements were added to pure iron in an effort to establish their effect on both hydrogen overvoltage and corrosion characteristics.

In oxygen-containing neutral solutions, such factors as composition, cold-work, and heat-treatment have little effect on the corrosion rate of iron and steels (2). The reason for this becomes obvious when one considers that the reaction, under these conditions, is cathodically controlled, and the corrosion current is essentially determined by the limiting diffusion current for oxygen reduction. In acid media, however, particularly when oxygen-free, the effect of the above factors may be pronounced. This is true because the metal is under mixed control in such an environment, and the corrosion rate is determined by both the anodic polarization characteristics and the hydrogen overvoltage behavior of the material. At present, there is no reason to believe that the local anodic polarization behavior of a steel is independent of composition. Hoar and Havenhand (3) have reported that local anodic polarization is the most important factor in determining corrosion rates of various steels in acid environments, but their conclusion is not completely supported by the present work. Their tests, unfortunately, were conducted in the presence of oxygen. Although the major anodic reaction is Fe (metal)$\rightarrow Fe^{++} + 2$ electrons, activation polarization for this anodic reaction could be quite different for different iron base alloys. For example, the site of the reaction should play a significant role, depending on whether dissolution occurs at grain boundaries, at specific crystallographic planes, or at various surface imperfections.[3] Anodic concentration polarization would probably be about the same for a variety of iron-base alloys and again would be roughly independent of composition and heat-treatment. Cathodic polarization (activation hydrogen overvoltage), on the other hand, should depend on metal structure and composition, and on impurities and depolarizers in solution (5).

It becomes obvious, therefore, that many factors influence the final corrosion rate of iron-base alloys in acids, but that all of these can be resolved into shifts and changes in local cell polarization behavior.

PROCEDURE

Using pure iron, which was the same material reported previously (1), alloys with the following composition were prepared: 0.11% copper, 0.08% silicon, 0.017% phosphorus, 0.02% sulfur, 0.11% manganese, 0.11% carbon, 0.11% manganese with 0.032% sulfur, 0.08% copper with 0.022% sulfur, and 0.10% copper with 0.028% phosphorus.

Alloys were melted in a vacuum induction furnace similar to that illustrated by Seybolt and Burke (6). The furnace was arranged so that additions to the melt could be made by magnetically moving a small pure iron cup containing the alloy addition down a Vycor chute into a pure alumina crucible containing molten iron.

Phosphorus was added as Bureau of Standards ferrophosphorus, while the carbon alloy was made by gas carburizing pure iron and adding a known quantity of the resultant material to molten iron. Other alloy additions were made with the purest elemental materials commercially available.

The 1 lb heats were cast in an iron mold using the stopper-rod bottom-pouring technique. The 1 in.

[1] Manuscript received March 17, 1955. This paper was prepared for delivery before the Pittsburgh Meeting, October 9 to 13, 1955.

[2] Present address: Metals Research Laboratories, Electro Metallurgical Company, Niagara Falls, New York.

[3] Hoar and Holliday (4) present an excellent discussion of the part surface structure plays on iron solution in acid media.

TABLE I. *Corrosion rates, corrosion currents, and hydrogen overvoltage constants in 0.1M citric acid (pH 2.06) at 25° C*

Alloy	Observed corrosion rate (mdd)	Corrosion potential E_{corr} (overvoltage scale)*	Tafel slope β	Exchange current i_o(μa/cm²)	Corrosion current i_{corr}(μa/cm²)	
					Calculated	Observed
Pure Fe	29	−0.172	0.084	9.3×10^{-2}	10.4	11.5
0.11% Cu	41	−0.175	0.081	1.0×10^{-1}	15.0	16.3
0.08% Si	45	−0.185	0.112	3.5×10^{-1}	15.6	18
0.017% P	165	−0.160	0.080	7.0×10^{-1}	70	66
0.11% Mn	18	−0.180	0.085	3.7×10^{-2}	5.0	7.2
0.015% S	706	−0.240	0.066	5.9×10^{-2}	258	282
0.11% C	710	−0.152	0.058	7.4×10^{-1}	310	284
0.11% Mn + 0.032% S	260	−0.225	0.086	2.9×10^{-1}	119	104
0.08% Cu + 0.022% S	32	−0.206	0.061	4.0×10^{-3}	9.6	12.9
0.10% Cu + 0.028% P	376	−0.141	0.021	3.0×10^{-5}	158	150

* Potential difference between alloy and hydrogen electrode in the same solution.

diameter ingots were machined smooth, cold-swaged to ½ in., and cold-rolled to 3/16 in.[4] The materials were then annealed 1 hr at 950°C, air-cooled, and machined into appropriate samples.

The procedures and equipment for determining corrosion potential, hydrogen overvoltage, and corrosion rate are the same as those reported previously (1). It is worth re-emphasizing here that, except where otherwise indicated, the data reported are steady-state values often obtained after waiting well over 100 hr.

Results

An earlier paper (1) discussed the cathodic behavior of pure iron in oxygen-free acid media. The role of both activation and concentration polarization was illustrated, and conditions necessary for elimination of concentration polarization were defined. The information which follows was accumulated under conditions where concentration polarization is negligible.

The earlier communication also discussed a method for calculating corrosion rates from electrochemical measurements alone. Briefly, this method is based on the assumption that corroding iron may be considered as a cathodically polarized hydrogen electrode with its own particular hydrogen overvoltage constants. The overvoltage constants and the corrosion potential define the local action current. The equation for local cathodic activation polarization as a function of current density is expressed

$$\eta_a = -\beta \log \frac{i_z + i_{la}}{i_o} \qquad (I)$$

where η_a = hydrogen overvoltage (activation), β = constant (slope of the Tafel region), i_z = external applied current density, i_{la} = local action current density, i_o = exchange current density.

With no external applied current (when the metal corrodes freely) the equation reduces to

$$E_{corr} = -\beta \log i_{corr}/i_o \qquad (II)$$

or

$$\log i_{corr} = \log i_o - E_{corr}/\beta \qquad (III)$$

where i_{corr} = corrosion current density and E_{corr} = corrosion potential on the overvoltage scale, i.e., difference in potential between an iron electrode and a hydrogen electrode in the same solution. (As used here, the potential is given a negative sign.)

Equation (III) reveals that an experimental determination of the corrosion potential, exchange current, and slope in the Tafel overvoltage region permits calculation of the corrosion current, i_{corr}.[5] Furthermore, equation (III) illustrates how various electrochemical factors affect the corrosion rate. High exchange current values, small β values, and active corrosion potentials contribute toward increasing the corrosion rate. As shown later, no one factor is more important than another in determining the final corrosion rate.

0.1M Citric acid (pH 2.06).—Table I gives corrosion data and overvoltage constants for the experi-

[4] The sulfur and manganese-sulfur alloys were too brittle to roll in this manner. The sulfur alloy was used as-cast, while the manganese-sulfur alloy was swaged to ¾ in. and rolled only to ⅜ in.

[5] For materials with very high corrosion rates, considerable current is necessary to polarize the electrode into the Tafel region to obtain β and i_o values. This sometimes gives difficulty from concentration polarization and resistance polarization effects. Where these difficulties were encountered, solutions were stirred with hydrogen gas to eliminate local surface *p*H increases. The resistance drop effect was corrected by progressively moving the salt bridge probe farther away from the electrode and extrapolating the *IR* drop thus obtained to zero distance. This procedure was checked by noting whether the resulting corrected data fell on a Tafel plot which is an extension of the straight line obtained in the lower current region where resistance drop is negligible.

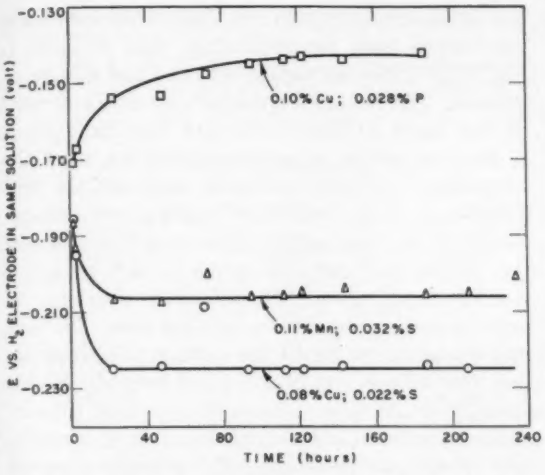

FIG. 1. Typical potential-time relationship for three steels in 0.1*M* citric acid (*p*H 2.06).

mental alloys in 0.1*M* citric acid. Also included is a comparison of corrosion currents calculated in the above manner and corrosion currents determined from actual rate measurements. The corrosion rate expressed in milligrams/square decimeter per day (mdd) is divided by 2.5 to obtain corrosion current in microamperes per square centimeter. It is evident that the electrochemical method appears to give reasonable checks with measured corrosion currents.[6] Overvoltage constants are markedly different for the various alloys, no one electrochemical factor being most important in influencing the rate.

Although electrochemical data presented in Table I are sufficient to describe the cathodic behavior of the alloys, detailed information for three of the materials is discussed below and may be considered typical. Fig. 1 and 2 illustrate the potential-time and weight loss-time curves for the copper-phosphorus, copper-sulfur, and manganese-sulfur alloys. Many of the alloys appeared to reach a steady corrosion rate after about 10 hr as was the case for the copper-sulfur alloy illustrated. The alloy containing sulfur alone never did quite reach a steady corrosion rate, the value increasing with time for reasons discussed later. The corrosion rate for the sulfur alloy reported in Table I is that determined at the time the cathodic polarization measurement was conducted—235 hr after the specimen was immersed.

Fig. 3 shows the overvoltage curves obtained for the above alloys and is used to illustrate how the various electrochemical factors influence the corrosion rate. It is well known that the corrosion rate is determined by the intersection of a local cathodic and a local anodic polarization curve. With this in mind, it becomes evident that shifting the local cathodic polarization curve to the right results in an intersection of local curves at a higher current value, producing a greater corrosion rate. This process is equivalent to increasing the exchange current, i_o. Further, if the local cathodic curve is made less steep, a higher corrosion rate results. This is equivalent to decreasing β in equation (I). Finally, a change in local anodic polarization behavior may cause either an increase or a decrease in corrosion rate; a decreased rate corresponds to a shift in corrosion potential in the noble direction, while an increased rate is accompanied by a potential shift in the active direction. Changes in local cathodic polarization behavior (changes in i_o and β) also affect the corrosion potential, and it becomes quite evident that there is no direct relation between corrosion potential

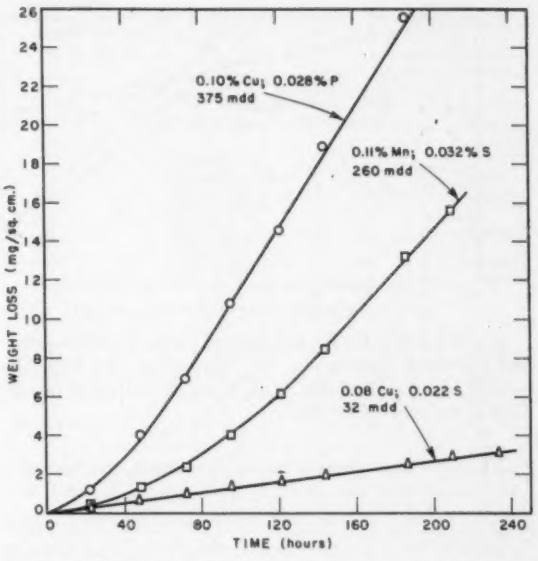

FIG. 2. Typical weight loss-time behavior of three steels in 0.1*M* citric acid (*p*H 2.06).

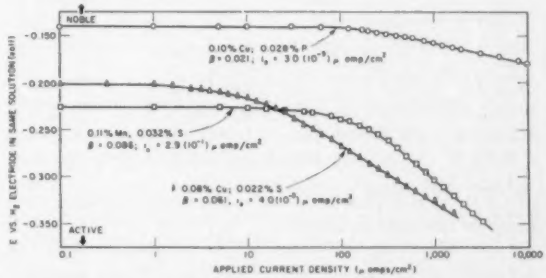

FIG. 3. Typical hydrogen overvoltage curves for three steels in 0.1*M* citric acid (*p*H 2.06).

[6] For 22 experiments with corrosion rates between 1 and 100 mdd, the average deviation between the two methods was found to be 12%. However, neglecting four runs with deviations greater than 20%, the average deviation becomes 7.8%.

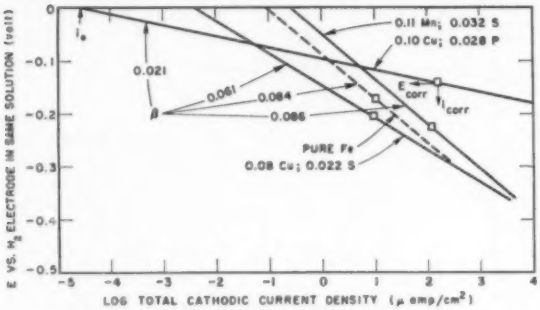

FIG. 4. Local cathodic polarization curves for three steels and pure iron illustrating the influence of the exchange current, i_o , and the Tafel slope, β, on the corrosion rate in 0.1*M* citric acid (*p*H 2.06).

TABLE II. *Corrosion rates, corrosion currents, and hydrogen overvoltage constants in 0.1M malic acid (pH 2.24) at 25°C*

Alloy	Observed corrosion rate (mdd)	Corrosion potential E_{corr} (overvoltage scale)*	Tafel slope β	Exchange current i_o (μa/cm²)	Corrosion current i_{corr} μa/cm²	
					Calculated	Observed
Pure Fe	3.0	−0.158	0.083	1.5×10^{-2}	1.2	1.2
0.11% Cu	0.9	−0.163	0.086	3.3×10^{-3}	0.26	0.36
0.08% Si	0.9	−0.176	0.088	2.2×10^{-3}	0.22	0.36
0.017% P	4.8	−0.168	0.097	3.7×10^{-2}	2.0	1.9

* Potential difference between alloy and hydrogen electrode in the same solution.

and corrosion rate for a series of alloys with different local polarization characteristics (Table I).

The overvoltage constants shown on Fig. 3 may be used further to illustrate how β and i_o affect rates. The copper-phosphorus alloy has an abnormally low exchange current, 3×10^{-5} μa/cm². Unfortunately, this advantage is more than compensated by a very low β value, 0.021. The net result is that the corrosion rate is still high. A comparison between the manganese-sulfur and copper-sulfur alloys shows that the manganese-containing material has the advantage of a high β value. However, this is overcome by the low i_o value of the copper-bearing material so that the corrosion rate for the latter alloy is lower.

Fig. 4 shows the local cathodic polarization curves[7] for these same alloys along with that of pure iron for comparison purposes. These local curves are constructed from the overvoltage data of Table I. Fig. 4 illustrates the various effects β and i_o have on the rate. The corrosion potentials are also indicated on this figure to illustrate a very important point. If the local anodic polarization curve for all of the alloys shown in Table I were the same, and the only difference between them were hydrogen overvoltage, then this one local anodic curve ought to intersect the various local cathodic curves in such a manner that the resulting corrosion potentials would fall on some smooth curve. This is not the case. The four points plotted in Fig. 4 are sufficient to illustrate this. Had all the data from Table I been put on this figure, it would be even more obvious that the corrosion potential is not a simple function of corrosion rate. Hoar and Havenhand (3) actually reported that various steels corrode at different rates in acids because the local anodic curves are different. Data reported here, however, actually show that both local anodic and cathodic polarization vary for different compositions.

0.1M Malic acid (pH 2.24).—Electrochemical data were obtained for only three of the alloys in 0.1*M* malic acid. This information is shown in Table II which includes data for pure iron reported previously. With few exceptions, the corrosion rates of the various alloys are considerably less in 0.1*M* malic acid than in either 0.1*M* citric acid or 4% sodium chloride at almost comparable *p*H values. Table II reveals that exchange currents in malic acid are considerably lower than in citric acid. This alone can account for a considerable portion of the rate decrease as explained earlier.

4% Sodium chloride (pH 1 and 2).—Table III gives electrochemical data for three alloys at *p*H 1 and 2. The alloys do not behave in the same manner as pure iron. The pure material appears to be practically independent of *p*H. For the alloys, however, both the Tafel slope and the exchange current are functions of *p*H. Table IV shows how the corrosion rate varies with *p*H for all of the alloys. No obvious explanation is available for the differences in behavior between pure iron and its alloys. Considerable research in the field of hydrogen overvoltage mechanisms is still necessary to explain such data.

DISCUSSION

The corrosion data of Table IV should be supplemented by some visual observations. The carbon

[7] Throughout the literature, reference is made to the fact that hydrogen overvoltage is a linear function of current at potentials only slightly removed from the reversible hydrogen potential. This is true if one plots overvoltage against applied current. For a hydrogen electrode, applied current is equivalent to the difference between the total rate of reduction of hydrogen ions and the total rate of oxidation of hydrogen gas. However, when one considers only the total cathodic current—equivalent to the total rate of hydrogen reduction—hydrogen overvoltage and a logarithmic function are so plotted in Fig. 4. A discussion of hydrogen electrode kinetics is given by Bockris (7).

TABLE III. *Corrosion rates, corrosion currents, and hydrogen overvoltage constants in 4% sodium chloride at pH 1 and 2*

Alloy	Observed corrosion rate (mdd)	Corrosion potential E_{corr} (overvoltage scale)*	Tafel slope β	Exchange current i_o(μa/cm^2)	Corrosion current i_{corr}(μa/cm^2)	
					Calculated	Observed
*p*H 1						
Pure Fe	30	−0.203	0.100	1.0×10^{-1}	10.5	11.1
0.11% Cu	390	−0.230	0.084	2.8×10^{-1}	154	156
0.08% Si	725	−0.230	0.089	6.7×10^{-1}	270	290
0.017% P	1000	−0.190	0.068	6.3×10^{-1}	390	400
*p*H 2						
Pure Fe	30	−0.201	0.100	1.1×10^{-1}	11	11.3
0.11% Cu	98	−0.233	0.093	1.3×10^{-1}	42	39
0.08% Si	89	−0.230	0.090	7.1×10^{-2}	28	36
0.017% P	480	−0.175	0.084	1.8	220	192

* Potential difference between alloy and hydrogen electrode in the same solution.

TABLE IV. *Corrosion rates of various alloys in oxygen-free acids at 25°C*

Alloy	NaCl *p*H 1	NaCl *p*H 2	0.1*M* Citric *p*H 2.06	0.1*M* Malic *p*H 2.24
Pure Fe	30	30	29	3.0
0.11% Cu	390	98	41	0.9
0.08% Si	725	89	45	0.9
0.017% P	1000	480	165	4.8
0.11% Mn	115	41	18	14.1
0.015% S	2830	244	706	151
0.11% C	562	220	710	488
0.11% Mn + 0.032% S	222	142	260	6.2
0.08% Cu + 0.022% S	186	162	32	168
0.10% Cu + 0.028% P	606	394	376	339

alloy corrodes by pitting; the sulfur alloy corrodes both intergranularly and at grain centers by pitting; and the samples of manganese-sulfur alloy pitted in 4 or 5 spots in all the environments except malic acid. The mechanical properties and the pitting tendency of this latter alloy indicate that all the sulfur was not completely combined with manganese. The copper alloy builds up a surface deposit of copper in sodium chloride solutions, while the phosphorus-containing materials corrode with a resultant black granular surface precipitate which was not identified. This black coating is not magnetite and was unstable when exposed to oxygen-containing distilled water, slowly turning to a white flocculent precipitate with traces of brown ferric hydroxide.

These results confirm earlier reports (3, 8, 9) on the detrimental effect that both phosphorus and sulfur have on corrosion rates in acids. Although early investigators unfortunately disregarded the important influence of oxygen in acid environments, their data still showed clearly the beneficial effect of copper in sulfur-bearing materials.

The overvoltage constants give some insight into why these elements affect the rate as they do. Phosphorus alone increases the exchange current. Sulfur functions by decreasing the Tafel slope, by changing the local anodic polarization characteristics, and by changing the anode to cathode area ratio. (This alloy pits.) Copper eliminates the detrimental effect of sulfur by lowering the exchange current. Both the sulfur and carbon alloys have two-phase structures which partly explains their pitting tendencies. Hoar (3) has reported that massive cementite is detrimental to acid corrosion resistance.

The effect of cation differences probably resides partly in their ability to complex iron and the added alloying elements. However, the significant differences in overvoltage constants for the same material in different environments indicates the cations or undissociated acid molecules play some role in the hydrogen reduction reaction.

In general, study of the various electrochemical constants shows the complex way in which the alloying elements affect overvoltage factors. Since only one composition of each alloy has been investigated and the interactions between various elements have not been fully explored, these data cannot be justifiably extrapolated to compositional effects in mild steel with normal quantities of foreign elements. Considerable additional information concerning the effects of various amounts of alloying elements and interactions between elements is important. Also, a study of the significance of hydrogen overvoltage measurements on a two-phase structure would be very helpful in interpreting data obtained on such complex metal surfaces.

Acknowledgment

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H. Uhlig were invaluable throughout the course of the work.

Any discussion of this paper will appear in a Discussion Section to be published in the June 1956 JOURNAL.

REFERENCES

1. M. STERN, *This Journal*, **102**, 609 (1955).
2. H. H. UHLIG, *Corrosion*, **5**, 169 (1949).
3. T. P. HOAR AND D. HAVENHAND, *J. Iron Steel Inst.*, **133**, 239P (1936).
4. T. P. HOAR AND R. D. HOLLIDAY, *J. Appl. Chem.*, **3**, 502 (1953).
5. J. O'M. BOCKRIS, "Electrical Phenomena at Interfaces," p. 155, The MacMillan Company, New York (1951).
6. A. U. SEYBOLT AND J. E. BURKE, "Experimental Metallurgy," p. 182, J. Wiley and Sons, New York (1953).
7. J. O'M. BOCKRIS, National Bureau of Standards Circular 524, p. 243 (1951).
8. C. A. EDWARDS, D. L. PHILLIPS, AND D. F. THOMAS, *J. Iron Steel Inst.*, **137**, 223P (1938).
9. J. E. STEAD, *ibid.*, **94**, 5 (1916).

An Electronic Self-Balancing Zero-Resistance Ammeter[1]

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ABSTRACT

A relatively simple electronic device is described which permits continuous observation of the short-circuit current flowing in a galvanic corrosion cell. The device is particularly useful for measuring currents from low-resistance cells, where the internal resistance of a micro- or milliammeter would be excessive. The corrosion cell current is automatically held at that value which maintains the cell voltage at 0 ± 0.00005v (50 μv).

INTRODUCTION

Measurement of short-circuit currents in galvanic corrosion cells has always posed a problem, since use of a series meter always introduces some additional resistance in the metallic circuit. This difficulty is not serious in high-resistance cells, since the additional resistance of a current meter is usually sufficiently low to be negligible. In low-resistance cells, however, introduction of a milliammeter or microammeter is frequently impractical.

The usual solution to this problem is the use of a so-called "zero-resistance" ammeter. The principle of the device has been presented by Brown and Mears (1). More recently, Godard (2) described a self-balancing zero-resistance ammeter which employed a relay-controlled, motor-driven potentiometric circuit, so arranged that the cell current was maintained at that value which produced zero voltage at the electrode terminals. Thus, *IR* drop in the entire metallic circuit was compensated exactly by an external voltage source.

The device to be described operates on the same basic principle as any zero resistance ammeter, but is felt to be considerably simpler than Godard's while retaining all the advantages of automatic balancing. In addition, the voltage-sensing system placed across the galvanic cell has a much higher input resistance than the sensitive relay used in Godard's meter. Thus, even high-resistance cells can be handled with no sacrifice of sensitivity at the balance point.

DESCRIPTION OF APPARATUS

Fig. 1 shows the basic circuit of a zero-resistance ammeter. To simulate short-circuit conditions, the current flow is adjusted to that value which produces zero voltage at the cell terminals. Such adjustment may be made by variation of R or of E. Godard's device operates by automatic adjustment of R; the device described herein operates by adjustment of E.

Fig. 2 shows the complete circuit diagram of the electronic zero-resistance ammeter. The basic cell circuit is at the lower left, and consists of a multirange ammeter (with a reversing switch), resistors R_1 and R_2, and terminals for an external recording meter (shorted when not in use), all connected in series. The voltage across R_1 is arranged to oppose the corrosion cell, while the voltage appearing across R_2 augments the cell. The remaining circuits are (*a*) a three-stage amplifier (top), (*b*) a phase detector (5963) which operates the relay, (*c*) parallel 6AK6's (bottom center) whose cathode resistor is R_2, and (*d*) a conventional power supply (lower right).

The operation of the device is as follows. When the current passing through the cell is such that the cell voltage is not zero, the 60-cycle chopper puts a pulsed signal on the grid of the first amplifier stage. This signal is amplified and applied to the grids of the 5963 phase detector. Depending on the polarity of the cell voltage, the signal will cause one or the other of the 5963 triode sections to conduct more heavily, depending on the phase relation between the signal and the a-c plate voltage. It should be noted that the voltages supplied to the two plates are 180° out of phase.

Depending on which triode conducts, a voltage is produced between the cathodes which moves the relay arm to the left or to the right. If it moves to the left, the control grids of the parallel 6AK6's are made more negative (toward cutoff); if it moves to the right, the grids are brought toward ground potential (increasing the tube current). As the 6AK6 plate current changes, the voltage drop across the cathode resistor (R_2) varies accordingly, thus increasing or decreasing the corrosion cell current, whichever is required to bring the cell voltage toward zero.

The amplifier gain is such that the device will hold the cell voltage at 0 ± 0.00005 v and will accommodate cell currents up to 20 ma.

Certain features of the circuit justify further comment. In order to compensate for the phase shift inherent in the chopper, its coil is placed in series with the 28 mfd condenser shown. This value was determined experimentally and was selected to make the point of switching coincide with the zero-voltage point in the 60 cycle a-c supply, thus providing maximum sensitivity in the phase detector.

[1] Manuscript received March 23, 1955.

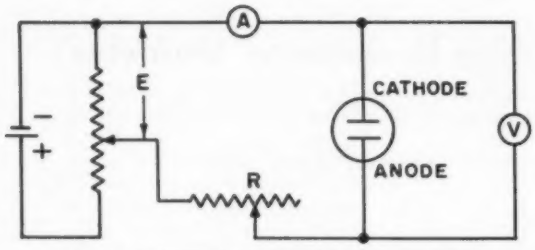

FIG. 1. Elementary zero-resistance ammeter

The 6.8 M and 10 M resistors in the grid circuit of the 6AK6's are not critical, but were selected to give reasonable rates of charge and discharge of the 1 mfd condenser. Smaller values of resistance would give a more rapid approach to the balance point, but would cause relay oscillation.

The purpose of the resistor R_1 and its associated circuit is to provide a fixed d-c voltage against which the 6AK6 cathode resistor can operate when only a very small voltage is required to drive the corrosion cell. Thus, the 6AK6 tubes always operate well above zero plate current, regardless of the actual corrosion current. This feature has the added advantage that cells whose polarity may reverse during a test can be observed continuously.

Resistors R_3 and R_4 in the cathode circuit of the 5963 are coarse and fine controls, respectively, for centering the relay position to correspond to zero corrosion cell voltage. Once set, no further adjustment is necessary.

The diodes of the 6AV6 amplifier tubes are unused; this tube was selected for the high amplification factor of its triode section. Type 12AX7 (dual triodes) should be equally satisfactory.

The chopper is a Model A-175, manufactured by the Airpax Products Company, which mounts in a 7-pin miniature socket. Its coil is operated from the 6.3 v heater supply.

The relay is a Model 534, manufactured by the

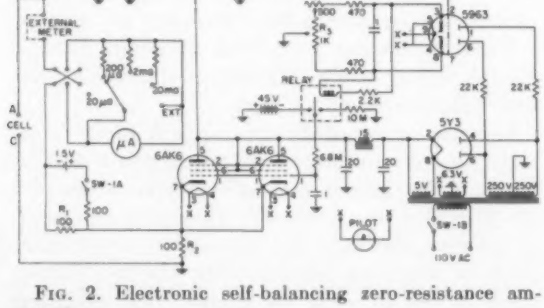

FIG. 2. Electronic self-balancing zero-resistance ammeter.

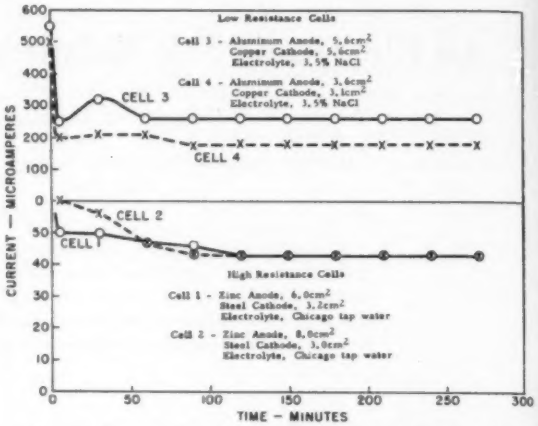

FIG. 3. Current flow in typical high- and low-resistance cells.

Weston Electrical Instrument Corporation; it has a sensitivity of -7.5 μa $-$ $+7.5$ μa, with a coil resistance of 1100 ohms.

The microammeter is a Triplett 321-T, with a range of 0–20 μa and a resistance of 2050 ohms. The range is extended by selection of the appropriate shunt resistor, as shown in Fig. 2. When an external recording meter is used, the internal meter may be shorted to minimize the total resistance of the cell circuit, if necessary. The exact values of the shunt resistors should be determined experimentally to insure accurate calibration of each current range.

TYPICAL DATA

To illustrate the operation of the device, a number of corrosion cells were made up and their current-time curves prepared. The results, together with the cell descriptions, are shown in Fig. 3.

While the range of currents embraced by the instrument could be extended above 20 ma if desired, this range seems adequate for most laboratory scale work.

Since most corrosion couples have open-circuit potentials in the order of many millivolts, the 50 μv sensitivity of the balancing circuit assures negligible departure from short-circuit conditions.

ACKNOWLEDGMENT

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REFERENCES

1. R. H. BROWN AND R. B. MEARS, *Trans. Electrochem. Soc.*, **74**, 510 (1938).
2. H. P. GODARD, *Corrosion*, **7**, 93 (March 1951).

Factors Affecting the Formation of Anodic Oxide Coatings in Sulfuric Acid Electrolytes[1]

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ABSTRACT

The amount of sulfate found in anodic coatings formed on pure aluminum anodes in sulfuric acid electrolytes increased as the current density and concentration of acid increased, but decreased as the temperature was raised. Chemical analysis showed that the coatings consisted substantially of Al_2O_3 and SO_3 with practically no water.

Factors affecting solubility of the coatings, such as heat developed within the coating, and time of immersion, were investigated. Rapid changes in current and voltage, which occurred in the first 15 sec after application of current, gave certain clues as to the possible mechanism of pore formation.

INTRODUCTION

In a paper by Norden (1) published only a few years after electrolytic aluminum became available in commercial quantities, the composition of sulfuric acid anodic coatings and the efficiency of the over-all electrochemical reaction were discussed. While some of the conclusions of that work are now considered to be in error, it was indicated even then that the oxide coatings formed in dilute sulfuric acid electrolytes contain about 13% SO_3 as determined by classical analytical methods.

Most investigators have recognized the presence of appreciable amounts of sulfate in anodic coatings formed in the sulfuric acid electrolytes. One aim of this paper is to show that the sulfate is an important minor constituent of the sulfuric acid anodic coating, and that the coating composition can be changed by varying the electrochemical conditions of formation.

Heat generated in an aluminum anode during coating, especially at high current densities, and the rapid changes in voltage and current which take place when the current is first applied to a clean aluminum anode in a sulfuric acid electrolyte were also investigated.

EXPERIMENTAL

Composition of Coatings

Specimens of 1095 aluminum, which had been preanodized in sulfuric acid, stripped in phosphoric-chromic acid, and weighed, were anodically coated in 15% sulfuric acid under varying conditions of time, current density, and temperature. They were then dried, weighed, and the coating removed in 50 ml of phosphoric-chromic acid stripping solution (2, 3). The water used to rinse each specimen was added to the stripping solution which was then diluted to exactly 100 ml. By weighing the specimens after stripping, it was possible to obtain by subtraction the exact weight of coating dissolved in the solution. Al_2O_3 and SO_3 were precisely determined in the same stripping solution containing an accurately known weight of coating.[2]

Conditions of forming the anodic oxide coatings, as well as the results of the analytical determinations, are shown in Table I. In the case of the 10-min coatings, three individual specimens were prepared and the oxide coatings removed in the same 50 ml of stripping solution. The 100 panels with the 5-sec coatings were formed individually and were weighed 10 at a time, but were all stripped in a single portion (50 ml) of stripping solution. It was necessary to concentrate the wash water by evaporation before adding to the stripping solution and diluting to 100 ml. For the control sample (or analysis blank), a volume of distilled water equal to the wash water was evaporated to slightly less than 50 ml and added to the stripping solution before diluting to the final 100 ml.

The Al_2O_3 and SO_3 content of the anodic oxide coatings prepared in 15% sulfuric acid at 70°, 50°, or 34°F (21.1°, 10.0°, or 1.1°C) accounted for practically the total coating weight. This meant that there could be little water present, at the most about 1%. Some coatings prepared at 50°F (10°C) were not dried at 105°C before stripping; consequently, they may have contained a small amount

[1] Manuscript received March 19, 1955. This paper was prepared for delivery before the Pittsburgh Meeting, October 9 to 13, 1955.

[2] The chromium was removed from an aliquot portion of the stripping solution in a mercury cathode cell before determining the aluminum. The sulfate was determined in the usual way from another portion of the stripping solution after reducing the chromate with alcohol.

TABLE I. *Composition of anodic oxide coatings on pure aluminum (1095)*

C.D.		Range volts	Time	No. panels	Panel area cm^2	Temperature		Total wt. coating g	Al_2O_3%	SO_3%	Total %
Amp/dm^2	Amp/ft^2					°C	°F				
1.3	12	23–23	30 Min.	1	77.4	1.1	34	0.2751	84.3	15.0	99.3
2.6	24	24–25	30 Min.	1	38.7	1.1	34	0.2834	84.4	15.9	100.3
3.9	36	25–27	30 Min.	1	25.8	1.1	34	0.2869	84.0	16.4	100.4
5.2	48	26–32	30 Min.	1	19.4	1.1	34	0.2946	83.3	16.8	100.1
7.8	72	27–42	30 Min.	1	12.9	1.1	34	0.3188	83.3	17.1	100.4
1.3	12		5.0 Sec.	100	77.4	10.0	50	0.0897*	88.6	13.9	102.5
1.3	12	20–20	10 Min.	3	77.4	10.0	50	0.2642*	86.0	13.7	99.7
1.3	12	20–20	10 Min.	1	77.4	10.0	50	0.0873*	85.3	13.6	98.9
1.3	12	20–20	30 Min.	1	77.4	10.0	50	0.2630*	85.3	14.1	99.4
1.3	12	20–20	30 Min.	1	77.4	10.0	50	0.2621	85.3	13.7	99.0
1.3	12	20–21	60 Min.	1	38.7	10.0	50	0.2625*	84.9	14.0	98.9
2.6	24	21–21	10 Min.	3	38.7	10.0	50	0.2741*	84.4	15.0	99.4
2.6	24	21–23	30 Min.	1	38.7	10.0	50	0.2727*	84.3	14.8	99.1
3.9	36	22–24	30 Min.	1	38.7	10.0	50	0.2769	84.0	15.3	99.3
5.2	48	23–23	10 Min.	3	19.4	10.0	50	0.2824*	83.4	15.9	99.3
5.2	48	23–27	30 Min.	1	19.4	10.0	50	0.2825*	83.9	15.9	99.8
7.8	72	24–26	10 Min.	3	12.9	10.0	50	0.2858	83.4	16.4	99.8
7.8	72	24–33	30 Min.	1	12.9	10.0	50	0.2968	82.5	16.8	99.3
7.8	72	23–37	30 Min.	1	12.9	10.0	50	0.2947	82.3	16.6	98.9
1.3	12	16–16	30 Min.	1	77.4	21.1	70	0.2395	86.1	12.4	98.5
2.6	24	19–20	30 Min.	1	38.7	21.1	70	0.2522	84.9	14.0	98.9
3.9	36	21–23	30 Min.	1	25.8	21.1	70	0.2596	84.7	14.8	99.5
5.2	48	21–23	30 Min.	1	19.4	21.1	70	0.2628	84.0	15.1	99.1
7.8	72	22–29	30 Min.	1	12.9	21.1	70	0.2712	83.3	16.0	99.3

Note: Electrolyte = 15% H_2SO_4.
* Coating not dried at 105°C before weighing and stripping.

of water sorbed on the surface. Oxide coatings prepared in sulfuric acid when only air dried contained a surprisingly small amount of water. Small analytical errors in the Al_2O_3 and SO_3 contents of the coatings formed at 34°F (1.1°C) are indicated, since the combined weights are slightly over 100%. The weight of aluminum reacting was no greater than

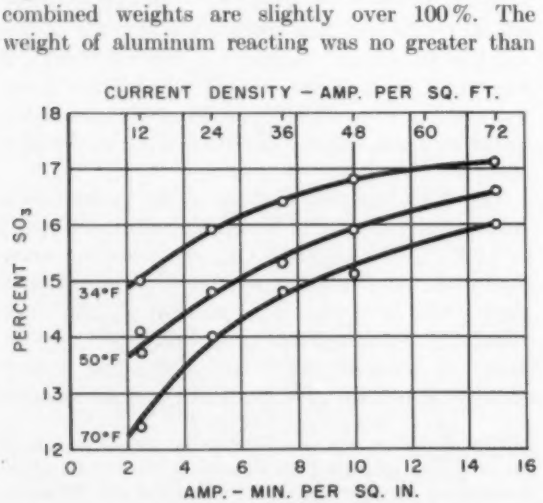

FIG. 1. Variation of SO_3 content with current density and temperature.

that demanded by Faraday's law, and the possibility of suboxide formation was considered. However, there was no reduction of the chromic acid in the stripping solutions that could be detected by the usual analytical methods.

Under corresponding conditions, the SO_3 content was higher at 34°F (1.1°C) than at 50° or 70°F (10° or 21.1°C). At a given current density, the percentage of SO_3 remained fairly constant as the thickness or weight of coating increased with time of treatment. When a higher current density was employed the SO_3 content rose.

Values for the 30-min coatings in Table I were plotted in Fig. 1 to show the uniform increase in SO_3 content with current density increase. Under corresponding conditions of current density, there was about 1.0% more SO_3 in the coatings produced at 34°F (1.1°C) than in those formed at 50°F (10°C).

Since the major constituents of the anodic coating formed in sulfuric acid on 1095 aluminum were (by chemical analysis) Al_2O_3 and SO_3, the weight ratio of Al_2O_3 to SO_3 was plotted against current density in Fig. 2. This type of plot minimized any error introduced by water sorbed on the oxide surface. At a weight ratio of 5.1 the composition corresponded to

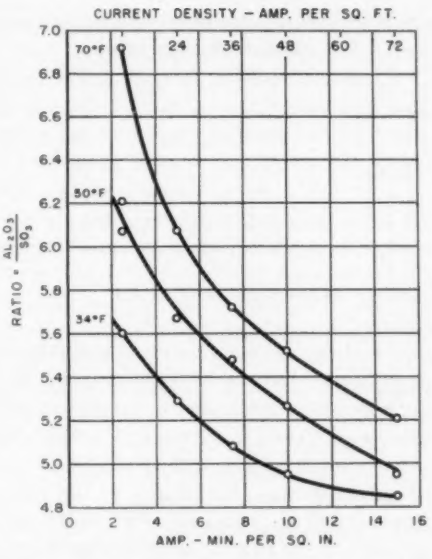

FIG. 2. Variation of the Al_2O_3:SO_3 ratio with current density and temperature.

$4Al_2O_3 \cdot SO_3$ or $Al_2(SO_4)_3 \cdot 11Al_2O_3$. However, the coating composition varied with the conditions of formation, and in most cases simple molecular formulas could not be assigned.

In Fig. 1 and 2, it should be pointed out that as the current density doubled, the thickness of the coating also approximately doubled. If the data for the coatings at 50°F other than the 30-min coatings in Table I were plotted in curve 1 according to the current densities employed, it would be found that the points would fall on or very near the curve already drawn. Therefore, it is concluded that current density and not thickness of coating controlled the SO_3 content of anodic coatings formed in sulfuric acid at a given temperature.

Oxide coatings formed on 1095 aluminum in 25% sulfuric acid at 50°F (10°C) had an appreciably higher SO_3 content than those formed in the 15% sulfuric acid. If plotted as the data of Fig. 1, the curve would lie slightly above the one for 34°F (1.1°C). In the case of coatings formed in an electrolyte of 12% sulfuric acid + 1% oxalic acid at 50°F (10°C), the SO_3 content was practically the same as that found for the 15% sulfuric acid electrolyte, but the coatings also contained about 0.2 to 0.4% oxalic acid. The higher value was obtained at the lowest current density, 12 amp/ft² (1.3 amp/dm²).

The sulfate incorporated in the oxide coating could not be removed by boiling in water or by the more drastic electroendosmosis treatment to an extent of more than about 2% of the total sulfate present. Only the sulfate actually exposed on the surface could be fixed as barium sulfate, and this again amounted to only 2% of the total amount present.

The sulfate content was a distinctive component of anodic coatings formed in sulfuric acid electrolytes.

TABLE II. *Heat effects at the aluminum anode*

Current density		Temperature rise			
		With agitation		Without agitation	
		°F	°C	°F	°C
amp/ft²	*amp/dm²*				
12	1.3	1.8	1.0	9.5	5.3
24	2.6	3.8	2.1	17.1	9.5
48	5.2	8.2	4.5	27.5	15.3

Heat Effects

In order to show that considerable heat developed in certain cases at the oxide-aluminum interface, a copper-constantan thermocouple was placed between two pieces of aluminum foil (1050) which were then cemented together. The cold junction of the thermocouple was placed in the 15% sulfuric acid bath at 50°F (10°C). Current was applied and a temperature reading made as soon as the voltage and current were constant. Temperature readings were made when there was good agitation of the electrolyte and when there was no agitation. Table II shows that, as the current density doubled, the temperature rise was about twice as great. It was also very evident that rapid agitation of the electrolyte was necessary for more effective removal of heat through the oxide surface.

As the time of anodic treatment at constant current increased, the voltage also rose, especially when high current densities were used. Two series of measurements are recorded in Table III to show how the temperature of the aluminum anode in these partic-

TABLE III. *Increase in temperature with time of treatment*

Current density		Time, min	Cell volts	Temperature rise	
				°F	°C
amp/ft²	*amp/dm²*				
48	5.2	1.5	24.0	7.9	4.4
		5	25.0	8.3	4.6
		10	26.0	8.5	4.7
		15	27.5	9.2	5.1
		20	30.0	10.7	5.9
72	7.8	1	25.0	8.6	4.8
		5	26.5	9.2	5.1
		11	33.0	11.8	6.5
		15	40.0	14.7	8.2
		20	48.5	18.1	10.1
		25	57.0	21.3	11.8
		30	68.5	27.4	15.2
		35	83.5	33.1	18.4
		40	110.0	42.9	23.8

ular experiments varied at constant current with time of treatment and voltage in the 15% sulfuric acid electrolyte at 50°F (10°C) with good agitation.

Results given in Table III show why it is impractical to treat a thin specimen, especially of 1050 metal, for a long time at a high current density even though good agitation of the electrolyte is used. Heat is developed very rapidly in the oxide coating and it can be removed only slowly by the electrolyte. Metallic aluminum is a good conductor of heat, and diffusion of heat takes place rapidly within the aluminum. By using a heavier gauge aluminum sheet as anode, the temperature within the oxide coating can be reduced. Some investigators have recommended internal cooling, but in many cases this is not a practical solution to the problem. If only a small area of a larger piece of aluminum is to be coated at 50°F (10°C), a resist can be used on the parts not to be coated, but the whole specimen should be immersed in the bath. If the part is exposed to the air at 70°F (21.1°C), heat will be carried into the specimen from without. The use of extra heavy insulated aluminum contacts or fins aids in the removal of heat from within the specimen.

Variations of Current and Voltage with Time

Although there are numerous references (4, 5) in the literature on oxide coatings showing the rapid changes in current and voltage which take place when a potential is applied to an aluminum anode immersed in a sulfuric acid bath, this work was repeated using the coating conditions employed for this paper.

Specimens of 1095 aluminum sheet, having the correct area to give the desired current density with 1 amp of current flowing, were suspended by tantalum clips midway between two lead cathodes in the vigorously stirred bath of 15% sulfuric acid at 50°F (10°C). A potentiometer across a bank of storage batteries was adjusted to give a final steady current of exactly 1 amp with a test specimen. A freshly cleaned specimen was then placed in the bath and the current applied. Readings were made at 1-sec intervals. About 10 freshly cleaned specimens were required for each curve, since only two or three points could be determined on one specimen. The average results of the current measurements were plotted against time in Fig. 3.

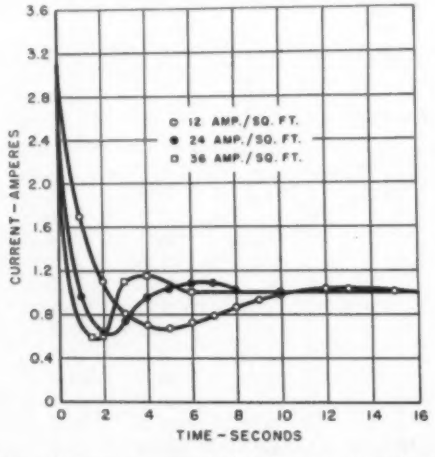

FIG. 3. Changes in current with time at the beginning of anodic oxidation. Current density values are for the steady state.

TABLE IV. *Variation of maximum and minimum voltages with current density*

Current density		Volts		
		Maximum	Minimum	Constant
amp/ft²	*amp/dm²*			
12	1.3	22.1 at 5 sec.	19.6 at 12 sec.	20.1
24	2.6	23.4 at 2-3 sec.	21.4 at 6 sec.	21.7
36	3.9	24.5 at 1-2 sec.	22.2 at 4+ sec.	22.5

Electrolyte temperature—50°F (10°C).

At the instant a potential was applied to a specimen, tested as above, there was a surge of current of about 3.3 amp. The current rapidly decreased to a minimum value of about 0.6 to 0.7 amp, the time required to reach the minimum value being dependent on the current density at the steady state. The current rapidly increased to a second maximum slightly greater than 1 amp and then fell to the steady current of 1 amp for which the potentiometer was originally set. The heights of the second maximum appear to be proportional to the current density. If agitation of the electrolyte was not used, the first portion of the curve was approximately the same, but the second maximum and the final steady current were higher.

When voltage readings were made as above, the voltage quickly reached a maximum corresponding to the time of the minimum current value and quickly decreased to a minimum voltage at the point where the current reaches the second maximum. The voltage then increased to a steady value corresponding to the steady current state.

The maximum and minimum voltages obtained for the aluminum-lead cell were recorded in Table IV.

The first portion of the 12 amp/ft² curve of Fig. 3, where the current decreased rapidly while the voltage rose, represented the formation of a fairly uniform film of increasing thickness and resistance. At this stage, the efficiency of oxide formation was less than 100% by the amount of oxide dissolved uniformly from the exposed outer surface by the sulfuric acid electrolyte. After about 4–5 sec the

formation of definite pores (4) started and continued with some adjustments in distribution until the steady state was reached in about 15 sec. At higher current densities the steady state was reached more rapidly and so the times given here are only relative, being dependent on the particular current source and potentiometer used.

The oxide coating composition was dependent on the current density, temperature, and composition of the electrolyte. The coating composition did not appreciably change after the initial 5 sec, provided the current density and temperature remained constant (see Table I).

After the pore pattern has been established, the solution of the oxide coating by the sulfuric acid is believed to be concentrated at the bottom of the pores, which all together represent an area of about one-ninth the apparent surface.[3] Because of the concentration of the sulfuric acid attack, the oxide at the bottom of the pores should be dissolved at a much more rapid rate—up to 9 times as fast. Part of the increased rate of solution at the bottom of the pores is believed to be the result of an increase in temperature. A more important factor may well be the more rapid solution rate of the electrolyte caused by discharged SO_4 ions or the products of this action. Regardless of the exact mechanism, the rate of solution of oxide at the bottom of the pores approximately equals the rate of oxide formation and the pore remains extending practically through the oxide coating. The outer portion of the coating, after the pore pattern is once established, is subjected only to the chemical solution action of the sulfuric acid at the average bath temperature. The efficiency of over-all oxide formation is always less than 100% by the amount of oxide dissolved in forming the pores and the small amount of oxide dissolved from the outer surface by chemical solution action of the sulfuric acid at the average bath temperature.

[3] The pore volume of a coating made under the above conditions is about 11%.

Summary

Oxide coatings formed in sulfuric acid were practically anhydrous but always contained an appreciable amount of combined sulfur. The composition of the coating may be represented as $Al_2O_3 \cdot XSO_3$ where X varies from about 0.18 to 0.26 depending on the conditions of formation.

Considerable heat was developed at the base of the pores, especially when high current densities were used. Unless this heat was removed rapidly through the oxide coating by suitable agitation of the electrolyte or by other means, the coating is dissolved at a more rapid rate.

The rapid changes in current and voltage that took place as the current was applied to an aluminum anode in sulfuric acid can be used to explain certain problems in regard to pore formation and the rapid solution of the anodic coating at the base of the pores.

Acknowledgment

Acknowledgment is made to Mr. Richard Unangst of the Aluminum Research Laboratories for his careful and painstaking analysis of the oxide coatings and to Miss Phyllis Fowle for the preparation of many of the specimens.

Any discussion of this paper will appear in a Discussion Section to be published in the June 1956 Journal.

REFERENCES

1. K. Norden, *Z. Elektrochem.*, **6**, 159, 188 (1899).
2. J. D. Edwards, *Am. Soc. Testing Materials, Proc.*, **40**, 959 (1940).
3. R. B. Mason and C. J. Slunder, *Ind. Eng. Chem.*, **39**, 1602 (1947).
4. W. Baumann, *Z. Physik*, **111**, 708 (1939).
5. V. H. Wilsdorf, *Z. angew. Physik*, **2**, 17 (1950).

Modified Calcium Pyrophosphate Phosphors[1]

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ABSTRACT

The preparation and optical properties of $(Ca,Na_2)_2P_2O_7$:Sb and $(Ca,Na_2)_2P_2O_7$:Sb:Mn phosphors are described. The partial substitution of sodium for calcium has been found to increase markedly the efficiency of the luminescent emission. The enhancement of luminescence as a result of this modification is attributed to compensation of valence: Sb^{+3} and Na^{+1} compensating for two Ca^{+2} in the lattice. The doubly activated phosphor provides an example of "sensitized luminescence." $(Ca,Na_2)_2P_2O_7$:Sb fluoresces in the deep blue. The observed fluorescence of $(Ca, Na_2)_2P_2O_7$:Sb:Mn may vary between blue-white and pink-white depending upon the manganese concentration.

INTRODUCTION

In recent years phosphors having an alkaline earth phosphate matrix have received considerable attention in the literature. Butler (1) described calcium orthophosphate activated by tin alone or by tin and manganese in combination. The study also included mixed orthophosphates of other alkaline earth elements. Froelich and Margolis (2) reported in detail on calcium orthophosphate doubly activated by cerium and manganese, and Froelich (3) studied magnesium pyrophosphate activated by combinations of cerium, thorium, and manganese. In the former case, sodium was found to enhance thermal stability; it did not contribute directly toward increased efficiency. Strontium orthophosphate activated by tin and manganese has been investigated by Botden (4). McKeag and Ranby (5) described calcium pyrophosphate activated by antimony, samarium, tin, or manganese, and Henderson and Ranby (6) developed an unusual phosphor, barium pyrophosphate activated by titanium in high concentrations. Huniger and Panke (7) surveyed a host of phosphate phosphors approximating metaphosphate proportions.

This paper describes the unusual effects obtained by the substitution of sodium for a minor portion of the calcium in calcium pyrophosphate phosphors activated by antimony alone or by antimony and manganese in combination.

PHOSPHOR PREPARATION AND COMPOSITION

Efficient $(Ca,Na_2)_2P_2O_7$ phosphors are conventionally prepared by a solid-state reaction involving firing an intimate mixture of (*a*) calcium monohydrogen phosphate (or the pyrophosphate), (*b*) a sodium compound such as the carbonate or a halide, (*c*) the activator compounds, and (*d*) enough ammonium phosphate to slightly more than compensate, on a molar basis, for the added sodium and activator ions. Treating a suspension of calcium and sodium carbonates and the activator compounds with phosphoric acid, drying and then firing the entire mass produces equally efficient phosphors.

Firing is carried out in an electrically heated furnace in open, fused silica trays. Generally, temperatures of from 850° to 875°C are employed, but the sodium concentration in the batch material governs the exact temperature: relatively high sodium requires relatively lower temperatures to avoid sintered products. The phosphors are white in body color with the exception that extremely high manganese concentrations produce a slightly pink powder.

Raw materials of at least reagent quality were used throughout the investigation. Calcium pyrophosphate phosphors appear to be comparable to the calcium halophosphates in sensitivity to the common "killer" impurities. The activators were generally introduced as Sb_2O_3 and $MnCO_3$, although any oxide-producing compound will serve, with the reservation that the products of decomposition do not contain metallic elements other than the specific activator elements.

As is true of many oxide-type phosphors, modified calcium pyrophosphate phosphors exhibit maximum efficiency when the composition departs from that of a stoichiometric compound. While generally described as pyrophosphates, maximum luminescence is only obtained when an excess of phosphate ion is present. If the base-to-acid ratio is defined as

$$\frac{\text{moles CaO} + \tfrac{1}{2}\text{ moles } Na_2O + \tfrac{1}{3}\text{ moles } Sb_2O_3}{\text{moles } P_2O_5}$$

then maximum luminescence occurs when this ratio falls between 1.85 and 1.95, as shown in Fig. 1.

Phosphors prepared without sodium are but

[1] Manuscript received June 27, 1955. This paper was prepared for delivery before the Chicago Meeting, May 2 to 6, 1954.

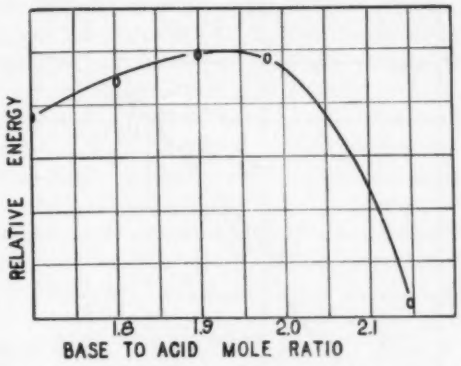

FIG. 1. Effect of base-to-acid ratio on relative energy output of (Ca, Na_2)$_2P_2O_7$:Sb under 2537 Å excitation.

weakly luminescent. Incorporation of a trace amount of sodium has a marked effect on the efficiency of the phosphor. Results show (Fig. 2) that the efficiency increases rapidly with increasing sodium, and less rapidly at about 0.5 mole % Na_2O. The optimum concentration is found to be about 0.8% Na_2O. Above the optimum, the brightness decreases only slightly; even at about 7% Na_2O, although highly sintered, the phosphor is still reasonably bright. The introduction of sodium has no effect on the color of the emission.

Antimony is incorporated in concentrations from about 0.1 to 1.5 mole % Sb_2O_3, although the more narrow range from 0.3 to 1% is preferred and about 0.7% gives maximum efficiency. Fig. 3 shows the effect of antimony concentration on relative efficiency of (Ca,Na_2)$_2P_2O_7$:Sb. The phosphors having a "white" emission, i.e., with manganese as well as antimony, generally require the same antimony concentration as do the singly activated blue-emitting phosphors. If manganese is added to the phosphor, its concentration should be controlled with some degree of accuracy in order to obtain the desired color (the reason for this is apparent from the data in Table III). The efficiency of the manganese band increases with concentration up to contents corresponding to 4.5 mole % $MnCO_3$. Higher concentrations reduce the intensity of the emission.

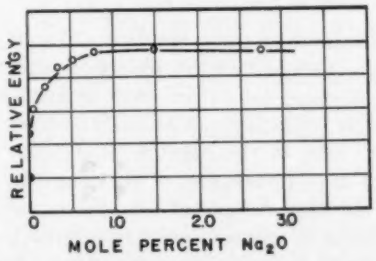

FIG. 2. Effect of sodium concentration on relative energy output of (Ca, Na_2)$_2P_2O_7$:Sb under 2537 Å excitation.

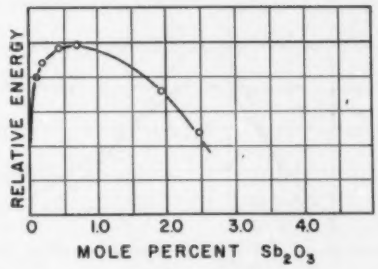

FIG. 3. Effect of antimony concentration on relative energy output of (Ca, Na_2)$_2P_2O_7$:Sb.

Table I gives representative formulations for three phosphors of varied emission spectra.

The sodium may, instead, be introduced as one of the halides or as any compound of sodium which converts to the oxide at the firing temperatures employed. The anion associated with the sodium cation has little effect on the optical characteristics of the phosphor.

Chemical analyses have shown that the only phosphor constituent lost during firing is antimony; generally about 10% of the added amount is volatilized. Virtually all of the antimony is present in the trivalent state, but a small amount is present in some acid-insoluble form, presumably a calcium antimonate.

Examination of x-ray diffraction patterns of (Ca,Na_2)$_2P_2O_7$:Sb phosphors has shown that sodium has no effect on the calcium pyrophosphate lattice. Antimony has been found to lower substantially the temperature of the beta to alpha inversion. Those phosphors having optimum composition and fired at temperatures which lead to high efficiency contain two phases: alpha and beta calcium pyrophosphate in approximately a 1:3 ratio. Firing temperatures of 1250°C lead to alpha modification pyrophosphate phosphors; these are mentioned below.

Emission Spectra-Optical Characteristics

(Ca,Na_2)$_2P_2O_7$:Sb phosphors are excited by short wave-length ultraviolet radiation (primarily 2537 Å Hg) to give a deep blue emission which has a peak wave length of 4150 Å. The position of this band in the spectrum is not affected by sodium concentra-

TABLE I. *Formulations of representative phosphors*

Component	Blue	Blue-white	Pink-white
	g	g	g
$CaHPO_4$	136.1	134.7	127.8
$(NH_4)_2HPO_4$	5.8	7.2	13.6
Na_2CO_3	1.3	1.3	1.3
Sb_2O_3	3.5	3.5	3.5
$MnCO_3$	0	1.1	6.9

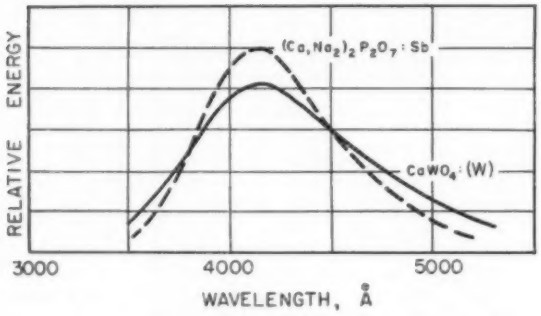

FIG. 4. Spectral energy distribution curves of (Ca, $Na_2)_2P_2O_7$:Sb and $CaWO_4$:(W) under identical conditions of excitation.

tion, nor by antimony concentration. The relative efficiency of the 4150 Å band, as influenced by the sodium concentration, is shown in Fig. 2. Fig. 4 shows the spectral energy distribution for the antimony-activated phosphor compared to self-activated $CaWO_4$ as excited by 2537 Å ultraviolet of the same intensity. The spectral energy distribution curves were obtained using a General Electric recording spectroradiometer.

The introduction of manganese, in addition to antimony, into the matrix gives rise to a new emission band with peak wave length of 5750 Å. At a fixed antimony concentration, with increasing manganese, the 5750 Å band continues to develop at the expense of the 4150 Å. Manganese alone produces a cathodoluminescent phosphor which fails to respond to 2537 Å ultraviolet. In Fig. 5 are shown the spectral energy distribution curves of several $(Ca,Na_2)_2P_2O_7$:Sb:Mn phosphors of variable manganese content. For comparison, a typical calcium halophosphate (about 1% manganese) is also shown. All the phosphors were excited by 2537 Å ultraviolet of equal intensity. Fig. 6 gives a portion of the I.C.I.

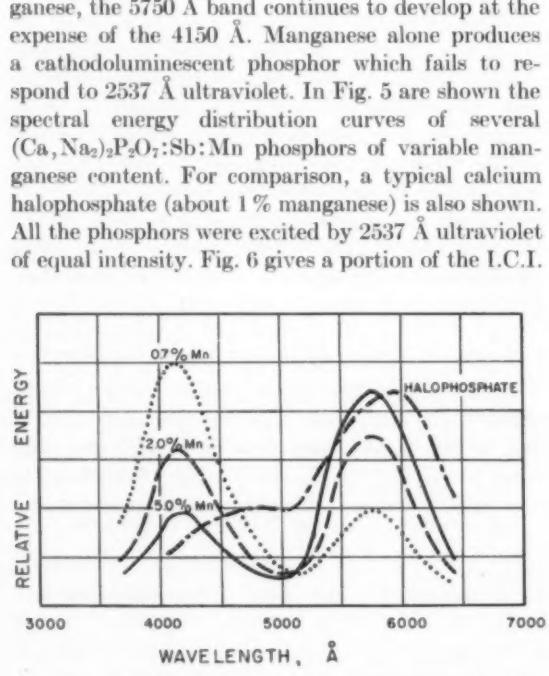

FIG. 5. Spectral energy distribution curves of (Ca, $Na_2)_2P_2O_7$:Sb:Mn phosphors of variable manganese concentration and a calcium halophosphate (1% Mn) under identical conditions of excitation.

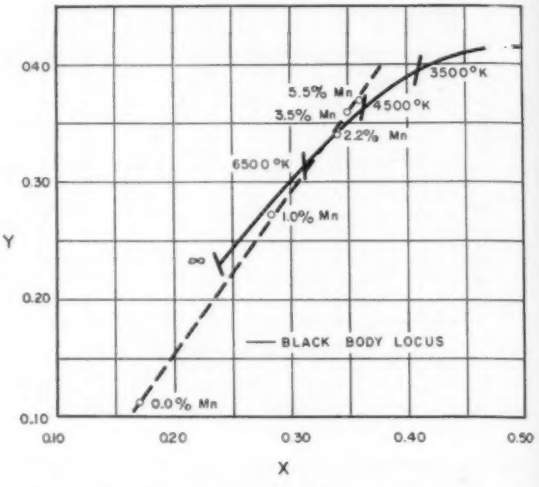

FIG. 6. I.C.I. coordinates x and y, for fluorescent lamps coated with various modified calcium pyrophosphate phosphors.

chromaticity diagram on which are plotted the trichromatic coefficients, x and y, for 40-watt fluorescent lamps coated with phosphors containing various concentrations of manganese. The values plotted are the average values for several lamps. The 100-hr luminous efficiency of these lamps varies between 13 lpw for the deep-blue-emitting $(Ca,Na_2)_2P_2O_7$:Sb and 42 lpw for $(Ca,Na_2)_2P_2O_7$:Sb:Mn prepared with about 2.5 mole % $MnCO_3$.

With cathode ray excitation the antimony (4150 Å) band of the singly activated phosphor is observed with moderate efficiency; the manganese (5750 Å) band of the doubly activated phosphor is excited more efficiently. Thus, the phosphor containing 2 mole % manganese and 1 mole % antimony is "white" under 2537 Å ultraviolet excitation, but a pronounced yellow-orange under cathode ray excitation.

The phosphorescence of the antimony emission decays at a faster rate than that of the manganese emission. Individual rates of decay are of the same order of magnitude as found for the respective emission bands in halophosphate phosphors.

Substitutions for Calcium

Substitutions of other divalent elements for calcium in $(Ca,Na_2)_2P_2O_7$:Sb phosphors shift the observed color toward longer wave lengths, but at a sacrifice of efficiency. With substitutions of the order of 10% of the calcium atoms, the shift is observed as a broadening of the long wave-length side of the 4150 Å band. When the ratio of atoms of substitute to atoms of calcium approaches unity, a new emission band becomes evident. Sodium is essential here to obtain optimum luminescence.

The introduction of cadmium gives rise to an emission band at 4600 Å which is detectable when 40% of the calcium atoms have been replaced. The relative efficiency of this band is about 50% of the original 4150 Å band, but the phosphor is 50% brighter due to increased eye-sensitivity in the 4600 Å region of the spectrum.

Similar observations were made for barium, strontium, zinc, and magnesium substitutions. Strontium, substituted for 60% of the calcium atoms, shows a rather weak band with a peak wave length of about 5000 Å. Barium gives a weak band with a peak wave length of about 5100 Å when 40% of the calcium atoms have been replaced. Magnesium and zinc substitutions both produce extremely weak emission bands.

These substitutions in $(Ca,Na_2)_2P_2O_7$:Sb:Mn phosphors serve to shift manganese emission toward longer wave lengths with lower efficiency. Magnesium, strontium, and zinc all reduce the efficiency so far as to be undesirable and the products of a barium substitution are nonluminescent, due to the insolubility of manganese in the presence of barium. Only cadmium produces a shift in peak wave length which results in practical efficiencies. When 25% of the calcium atoms have been replaced by cadmium, the manganese band has a peak wave length of 5850 Å.

Sensitized Luminescence

The $(Ca,Na_2)_2P_2O_7$:Sb:Mn phosphors are an example of "sensitized luminescence," a phenomenon recently afforded considerable treatment in the literature, in particular by Botden (4), Schulman (8), Ginther (9), and Fonda (10) on specific luminescent systems, and by Dexter (11) on some theoretical aspects. Measurements of quantum outputs of the sensitizer and activator emission bands relative to the quantum output of magnesium tungstate which has been shown (12) to have a conversion efficiency of 100% were made for phosphors of variable antimony and manganese contents. Table II summarizes the effects of variations in antimony concentration on the quantum outputs of the two emission bands for phosphors containing a fixed activator content of 2.6 mole % as manganese carbonate. Under the same conditions of excitation, magnesium tungstate is arbitrarily assigned a quantum output of 100.

TABLE II. *Effect of* Sb_2O_3 *concentration on quantum outputs*

Mole % Sb_2O_3	Quantum output Sb	Quantum output Mn	Total Quantum output	Ratio quantum output Mn/Sb
0.01	5.0	8.4	13.4	1.68
0.06	12.9	25.2	38.1	1.95
0.26	19.7	32.4	52.1	1.65
0.55	20.4	37.3	57.7	1.83
0.96	19.9	35.1	55.0	1.77
1.20	18.7	33.9	52.6	1.82
2.46	16.2	32.5	48.7	2.00

TABLE III. *Effect of* $MnCO_3$ *concentration on quantum outputs*

Mole % $MnCO_3$	Quantum output Sb	Quantum output Mn	Total quantum output
0	55.4	0	55.4
0.04	43.5	13.0	56.5
0.50	38.0	21.0	59.0
1.28	31.6	31.6	63.2
2.36	23.5	40.0	63.5
4.27	15.7	44.0	59.7
6.90	11.7	38.5	50.2
9.53	8.7	28.8	37.5

The effects of increasing manganese content on the quantum outputs of the two emission bands, at a fixed sensitizer content of 0.4 mole % antimony trioxide, are given in Table III.

It is apparent that the quantum outputs of both the sensitizer and activator emission bands rise with increasing sensitizer content until an optimum is reached, in this case about 0.7 mole % Sb_2O_3. With increasing activator content, the quantum output of the sensitizer emission falls continuously, whereas the quantum output of the activator emission rises to an optimum at about 4.5 mole % $MnCO_3$.

Critical concentrations of sensitizer and activator for optimum output of the phosphor system are about 0.7 and 5 mole %, respectively. At these concentrations phosphors have been prepared with total quantum outputs of about 65. The best phosphors have absolute absorptions for short wave-length ultraviolet of about 77%. The internal quantum efficiency (conversion of absorbed short wave-length ultraviolet to emitted visible radiation) is therefore about 80%, based on magnesium tungstate having 95% absolute absorption and an internal quantum efficiency of 100%. The singly activated phosphor has an internal quantum efficiency of about 80% also.

If the ratio of the quantum outputs of the activator and sensitizer emissions as a function of sensitizer concentration is considered (Table II), this ratio is found to be independent, within the limits of experimental error, of the sensitizer concentration. This is taken as evidence that the transfer of energy from an excited sensitizer center to an activator center is a direct, one-step process. The transfer of energy to an activator center takes place only when activator centers are in close proximity to sensitizer centers. Maximum quantum output occurs when the ratio of activator concentration to sensitizer concentration is high; in this case 7:1. This direct transfer process

is identical to that found in CaF_2:Ce:Mn phosphors (9) where maximum efficiency of the process occurs at an activator to sensitizer ratio of 10:1. This is in contrast to the character of the energy transfer in $Ca_3(PO_4)_2$:Ce:Mn (4) and 3 $Ca_3(PO_4)_2$:CaF_2:Sb:Mn (10) where the ratio of the quantum output of the activator to that of the sensitizer increases with sensitizer concentration. This is interpreted as denoting that the transfer may involve a succession of sensitizer centers before the energy is eventually transferred to an activator center. In these latter cases, the ratio of the critical concentrations of activator to sensitizer approximates unity. The distinctive differences among sensitized phosphors are treated fully by Botden (4).

The range of transfer of energy from sensitizer to activator may be calculated according to the relationship (4, 8, 9)

$$\frac{\text{Quantum Output Mn}}{\text{Quantum Output Sb}} = \frac{1 - (1 - X_{Mn})^k}{(1 - X_{Mn})^k}$$

where X_{Mn} is the activator concentration. Assuming an average value for the ratio of quantum outputs of 1.8 and a concentration of activator equal to 2.6 mole % $MnCO_3$, the range over which energy is transferred, K, is 39 atoms. This is in agreement with experimentally determined values for other systems (4, 8, 9) as well as the theoretically predicted value (11).

Discussion

Substitution of a minor portion of the calcium by sodium in calcium pyrophosphate phosphors activated by antimony alone or by antimony and manganese in combination has been shown to increase greatly the efficiency of these phosphors. The role that sodium plays in producing the observed effects is not fully understood and can, at best, only be subjected to hypothesis.

On the basis of Kroeger's (13) explanation for the function of halide in ZnS:Ag phosphors, it is suggested that monovalent sodium ions fill the lattice vacancies that would ordinarily arise from the replacement of divalent calcium ions by trivalent antimony ions. Thus, one monovalent sodium ion and one trivalent antimony ion replace two divalent calcium ions in the lattice, and electroneutrality is preserved. Maximum luminescent efficiency should then occur when the number of antimony ions and sodium ions is equal. This has been shown to be the case. That high efficiency is maintained when sodium ions are present well in excess of the number required for electroneutrality is ascribed to a fluxing action, in the true sense, on the part of the sodium ions. It is quite probable that additional sodium ions occupy interstitial sites. Sodium oxide or a sodium halide might well exist in solid solution in calcium pyrophosphate, particularly in fairly low concentrations.

TABLE IV. *Ionic radii of elements*

Monovalent		Divalent		Trivalent	
	Å		Å		Å
Li	0.60	Mn	0.90	Sb	0.90
Na	0.98	Ca	0.99		
K	1.33	Cd	0.97		

It might be supposed that any monovalent cation could function in the manner described for sodium. The size of the other alkali metal ions, relative to divalent calcium, precludes their filling the lattice vacancies without considerable effect on the lattice dimensions and the lattice position of the antimony centers, or, possibly, their ionic radii are so divergent that they are insoluble in the lattice. It is also an observed fact that lithium and potassium do not bring about the pronounced increase in luminous output that sodium does. Table IV gives the ionic radii (due to Goldschmidt or Pauling) of several pertinent elements.

The addition of manganese to the system presents no problem since Mn^{+2} and Ca^{+2} are mutually interchangeable.

While $Ca_2P_2O_7$:Sb phosphors absorb a fair amount of short wave-length ultraviolet, they are not efficient. The introduction of sodium, however, greatly increases the absorption and the resulting light output. $(Ca,Na_2)_2P_2O_7$ is not a good absorber and does not exhibit luminescence.

Kroeger and co-workers (14) have noted that the position of the emission band for $Ca_2P_2O_7$:Mn under cathode ray excitation depends on the temperature of preparation. These investigators report that the beta modification, obtained by firing below 1150°C, has an emission with peak wave length of about 5650 Å, and the alpha modification, obtained by firing above 1150°C, has an emission with peak wave length of about 6000 Å. In the present investigation, phosphors were generally prepared at temperatures well below the range from 1150° to 1270°C, the range of reported temperatures for the transition from beta to alpha calcium pyrophosphate. The peak wave length of the manganese emission in $(Ca,Na_2)_2P_2O_7$:Sb:Mn phosphors, excited either by short wave-length ultraviolet radiation or by cathode rays, is 5750 Å or slightly higher than Kroeger's value. This is attributed to the presence of some alpha pyrophosphate in a predominately beta system as has been shown by x-ray analyses.

$(Ca,Na_2)_2P_2O_7$:Sb:Mn phosphors fired at temper-

atures of about 1250°C exhibit emission bands with peak wave lengths of 4400 Å and 6000 Å for the antimony and manganese bands, respectively. These phosphors are badly sintered and not as efficient as those prepared at 850°–875°C.

Acknowledgment

The author wishes to thank Shannon Jones and Dr. Gorton R. Fonda for their many helpful discussions. He wishes to acknowledge the interest and encouragement of Walter P. Cartun, Richard S. Mackie, and the late P. R. Dickinson. Finally, the author is indebted to his colleagues in various departments of the Lamp Division and in the Research Laboratories of the General Electric Company for their varied contributions and assistance without which this investigation would not have been possible.

Any discussion of this paper will appear in a Discussion Section to be published in the June 1956 Journal.

References

1. K. H. Butler, *This Journal*, **100**, 250 (1953).
2. H. C. Froelich and J. M. Margolis, *ibid.*, **98**, 400 (1951).
3. H. C. Froelich, *ibid.*, **95**, 255 (1949).
4. Th. P. J. Botden, *Philips Research Rpts.*, **7**, 197 (1952).
5. A. K. McKeag and P. W. Ranby (To General Electric Co., Ltd.) British Pat. Spec. 578,272, June 21, 1946.
6. S. T. Henderson and P. W. Ranby, *This Journal*, **98**, 479 (1951).
7. M. Huniger and H. Panke (To General Electric Co.), U.S. Pats. 2,241,950, May 13, 1941; 2,241,951, May 13, 1941; 2,270,124, Jan. 13, 1942.
8. J. H. Schulman, R. J. Ginther, and C. C. Klick, *This Journal*, **97**, 123 (1950).
9. R. J. Ginther, *ibid.*, **101**, 248 (1954).
10. G. R. Fonda, *Brit. J. Appl. Phys.*, Supplement No. 4, 69S (1955).
11. D. L. Dexter, *J. Chem. Phys.*, **21**, 836 (1953).
12. G. R. Fonda, *J. Phys. Chem.*, **49**, 303 (1944).
13. F. A. Kroeger and J. A. M. Dikhoff, *Physica*, **16**, 297 (1950).
14. F. A. Kroeger, J. Th. G. Overbeek, J. Gorrison, and J. Van den Boomgaard, *This Journal*, **96**, 132 (1949).

The Enhancement Effect of Electric Fields on Some X-Ray Excited Phosphors[1]

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ABSTRACT

Further experiments are reported on the enhancement of phosphor output by the application of an electric field. This new and permanent enhancement of the light emitted by phosphors irradiated by x-rays is different from the momentary illumination observed in the Gudden and Pohl effect. Many factors have been studied, such as field strength, frequency, and temperature.

INTRODUCTION

Some years ago it was reported (1) that electric fields could produce a quenching of light emitted by some phosphors (such as ZnS:Cu, ZnSCdS:Ag, ZnSCdS:Cu) when these phosphors were irradiated either by x-rays or by ultraviolet radiations. Since that time, many additional results have been published on this phenomenon which is observed when the phosphor powder, embedded in an insulator, is suitably excited between two electrodes, one of which is transparent (conducting glass).

More recently (2) an opposite phenomenon was reported. It was observed when some ZnSCdS:Mn phosphors were irradiated by a beam of x-rays. It also occurred with some ZnS:Mn phosphors, but to a lesser degree. When the field was applied simultaneously with irradiation by x-rays, the light emitted by this phosphor was greater than when no field was applied.

DESCRIPTION OF PHENOMENON

Schematically, when no field was applied, the brightness, excited only by the action of a constant beam of x-rays, increased with time following curve I or OAB (Fig. 1). If, simultaneously with the x-ray irradiation, an alternating field was applied (not a constant field in order to avoid polarization effects), the brightness increased, following curve II which lies higher than curve I.

Let B_0 and B_1 be, respectively, the constant brightness reached after a certain time when no field is applied (curve I) and when the field is applied (curve II). The ratio $r = B_1/B_0$ is then called the "sensitizing ratio." It can reach values higher than 3.

If the phosphor was irradiated from time zero, but the field was not applied until time t_1, the brightness first increased following the part OA of curve I, at time t_1 it rose suddenly following AM, and then it decreased slowly toward the plateau of curve II. If the field was then removed at time t_2, one again observed a sudden rise PQ and the brightness then fell again slowly toward the plateau of curve I. The small peaks M and Q must be ascribed to a small Gudden and Pohl effect (3).

The phenomena were quite different when the above phosphors were irradiated by ultraviolet radiations instead of x-rays. In this case the usual quenching effect was observed, that is to say a curve II below curve I.

Cusano (4) recently found a similar phenomenon of enhancement when thin transparent layers of some phosphors, but not powders, were placed between two electrodes in contact with the sensitive layer. With such a device Cusano observed that there was always an enhancement of the emission when a direct field was applied, irradiation being either by x-rays or by ultraviolet radiations.

All experiments reported here were made on powders embedded in an insulator and subjected to an alternating field.

Field dependence of the sensitizing ratio.—Very low fields, even 200 v/cm, were able to give a noticeable effect. The sensitizing ratio first increased with the field strength and then passed through a maximum at about 15,000–20,000 v/cm (Fig. 2). On the same figure are shown, for the same phosphor, the variations of the "quenching ratio" when irradiation is made by ultraviolet radiation instead of x-rays.

Effect of frequency and x-ray beam intensity.—Experiments have been made between 10 and 5,000 cps. In this range, the sensitizing ratio was not dependent on the frequency of the applied field.

Similarly, the sensitizing ratio was not dependent on the intensity of the exciting beam. Using an x-ray

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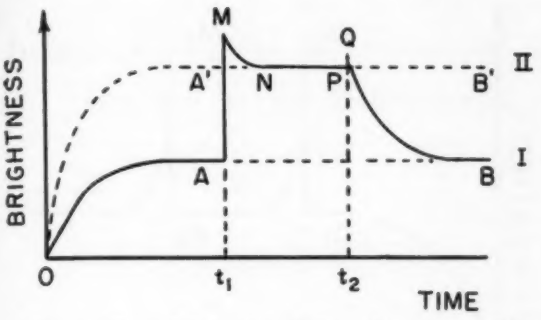

FIG. 1. General behavior of the enhancement effect. Curve I (*OAB*) when no field is applied; Curve II (*OA'B'*) when a field is applied, from time zero, simultaneously with x-ray irradiation. If the field is applied at time t_1 a sudden rise *AM* is obtained and another small rise *PQ* when the field is removed.

half-wave generator (80,000 v applied to the tube), the sensitizing ratio varied only 6% when the tube current was varied from 0.1 to 1 ma.

Effect of temperature.—When the temperature was raised from 18° to 54°C, the brightness B_0 and B_1 (the plateaus of curves I and II, respectively) both decreased, but the sensitizing ratio, r, remained almost constant. Table I gives data on one representative sample. In this narrow temperature range the variations of r are near the limit of the experimental error.

TABLE I

Temperature °C	B_0 (arbitrary units)	B_1 (arbitrary units)	Sensitizing ratio r
18	115	172	1.50
23	107	160	1.50
29	99	147	1.48
37	82.5	125	1.51
42	80	118	1.48
45	75	112	1.49
49	70.5	104	1.48
52	71.5	105	1.47
54	67.5	99	1.47

Brightness Waves

It has been shown (5) that, in the quenching effect, brightness waves (instantaneous output as a function of time during a cycle of field variation) were deeply disturbed, chiefly by the appearance of a secondary and transient peak at the time when, in each cycle, the field passed through zero. In the enhancement effect, however, although the height of each peak is increased, the shape of the brightness wave was generally only very weakly disturbed, and with some samples there was no disturbance. With other samples which showed some very small disturbances of the brightness waves in the enhancement effect, however, the same behavior of a transient but very small secondary peak on the decreasing side was found; this peak always occurred at the time when the field, in each cycle, passed through zero (Fig. 3).

Identical phenomena occurred when the half-wave x-ray generator was operated at a frequency twice that applied to the electroluminescent cell in order to obtain one emission of light in each half-cycle of the field variation.

With doubly activated phosphors (for example, Cu and Mn activated ZnSCdS) a Gudden-Pohl effect can be superimposed on the normal enhancement effect (Fig. 4), but this flash lasts only a very short time. It is thus quite different from the permanent phenomenon described above.

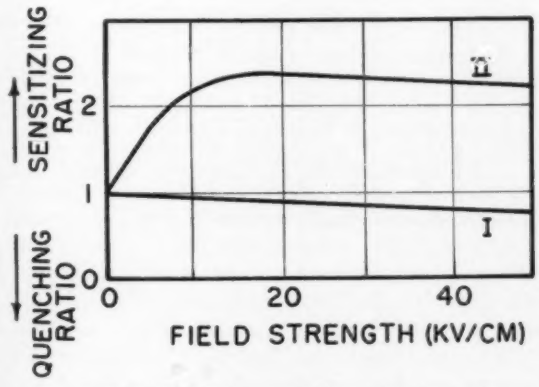

FIG. 2. Variations of the quenching ratio (curve I) as a function of field strength when irradiation is made by ultraviolet radiation, and variations of the sensitizing ratio (curve II) when irradiation is made by x-rays. The phosphor sample is the same in both cases.

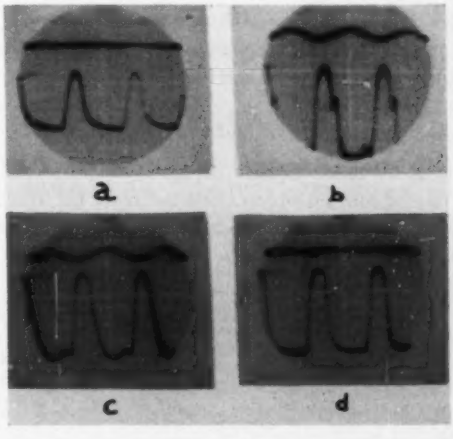

FIG. 3. Brightness waves for sample No. 1 of low sensitivity; simultaneous recordings of sinusoidal field wave and brightness wave (upper trace in each is sinusoidal field): (*a*) without any field; (*b*) at the time of the greatest disturbance (with secondary peak); (*c*) after a long time; (*d*) when the field is removed.

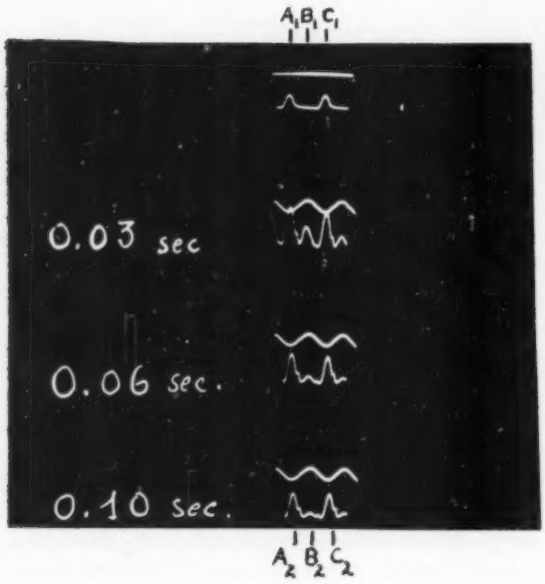

FIG. 4. Mn and Cu activated ZnSCdS. Superimposition of a Gudden and Pohl effect on the enhancement effect. Beam of x-rays emitted from a half-wave x-ray generator. Upper recording: brightness wave just before field application; second recording: 0.03 sec after field application; third recording: 0.06 sec after field application; fourth recording: 0.10 sec after field application. On vertical lines A_1A_2 and C_1C_2 brightness waves of an enhancement effect plus a quickly decreasing Gudden and Pohl effect. On vertical lines B_1B_2 only the brightness wave of the Gudden and Pohl effect, the intensity of which vanishes quickly.

Effect of a Constant Field

When a direct potential is applied to such a cell without contact between the crystals and the electrodes, the internal field strength starts from a certain value E and then decays following an exponential law with time constant

$$\theta = 4\pi/K\rho$$

where K is the dielectric constant and ρ is the resistivity of the phosphor. Similarly, at the removal of the direct potential, the internal field immediately starts from the same value E and then decays following the same exponential law.

In both cases, i.e., when the constant potential is applied or removed, the internal field, which is the effective field in the crystals, starts from the same value and quickly falls toward zero. With such a device, one can obviously obtain only a momentary enhancement when the constant potential is removed as well as when it is applied (Fig. 5).

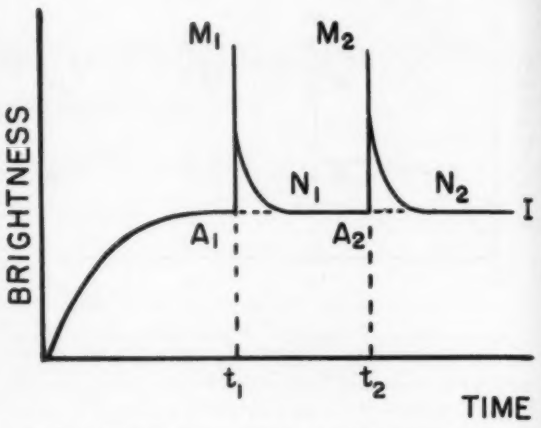

FIG. 5. Effect of a constant electric field upon the brightness of a phosphor excited by x-rays. Only a flash occurs at time t_1 when a d-c potential is applied, and another flash at time t_2 when the field is removed.

CONCLUSIONS

The light emitted by some Mn-activated ZnSCdS and also by some Mn-activated ZnS irradiated by x-rays is enhanced under the action of an electric field, while the light emitted is quenched by the field when irradiation is made with ultraviolet radiation. This phenomenon of permanent enhancement is quite different from the flash of momentary illumination observed in the Gudden and Pohl effect.

Any discussion of this paper will appear in a Discussion Section to be published in the June 1956 JOURNAL.

REFERENCES

1. G. DESTRIAU, *J. phys. radium*, **4**, 32 (1943).
2. G. DESTRIAU AND M. DESTRIAU, paper presented at ECS Chicago Meeting, Abstract 45, May 2–6, 1954.
3. B. GUDDEN AND R. W. POHL, *Z. Physik.*, **2**, 192 (1920).
4. D. A. CUSANO, paper presented at meeting of the American Physical Society, New York City, Abstract LA6, January 1955.
5. G. DESTRIAU, *J. Appl. Phys.*, **25**, 67 (1954).

Influence of the K Absorption Edges of Cadmium and Silver on the X-ray Diffraction Patterns of Some Cadmium Compounds[1]

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ABSTRACT

On x-ray powder and single-crystal rotation photographs of CdS, CdSe, and CdO, certain low-angle spots and lines were observed. Analysis of the absorption conditions of the general radiation showed that the unique closeness of the K absorption edges of Cd in the sample and Ag in the film emulsion could form a spectral line. The low-angle lines thus appear as Bragg reflections of the crystals of these substances produced by an average wave length $\lambda = 0.475$ Å.

Introduction

X-ray powder and single-crystal rotation photographs of CdS obtained by Ni-filtered CuKα radiation show relatively sharp lines or spots in the low-angle region in addition to the pattern of hexagonal CdS. In a previous paper (1) the low-angle diffraction effects of the two substances were tentatively related to one of the following: presence of an unknown modification, stacking faults, or deformation faulting in the crystals.

Observations of discontinuities due to absorption effects on the x-ray diffraction photographs of Mo and Sb (2) suggested that similar conditions could affect Cd compounds. In general, the white radiation of the Cu target x-ray tube which passed through the Ni filter produced only a continuous background on the film, i.e., the Ag absorption edge was usually masked. Absorption of radiation in the sample, however, caused discontinuities at the particular wave lengths which corresponded to the absorption edges characteristic for the elements in the sample material (3).

An abrupt change of the reflected intensity occurred in the band of white radiation for the wave length corresponding to a K absorption edge, where the absorption coefficient changed in the ratio of approximately 8:1. Bragg reflections of single crystals or crystal powders were thus caused by the white radiation and were reflected to definite angles, which introduced steps in the background of the film. As a rule, such discontinuities on the film did not have the appearance of a single crystal spot or a Debye-Scherrer line, but they looked like bands (4). Furthermore, the prominence of the steps was reduced by scattered radiation from all parts of the x-ray equipment and by Compton scattering of the sample. However, if the sample contained elements having a K absorption edge close to that of the Ag grain in the emulsion, an additional absorption effect contributed to the contrast of the steps. The Cd (at. no. = 48) K absorption edge at 0.4641 Å lay very close to that of Ag (at. no. = 47), λ_K = 0.4858 Å. At the Ag edge, a sudden increase of the sensitivity of the photographic emulsion occurred for the remaining part of the white radiation band reflected by the crystallographic planes of the Cd-containing sample but not absorbed by the Cd in the sample. Cd in the sample and Ag in the film emulsion therefore formed a selective filter so that only a thin band was observed with an average wave length of 0.475 Å. Because of the unique closeness of the K absorption edges of the two elements, the spectral width of the band appearing on the film was very narrow (0.022 Å). The resulting effect, in a sense, was comparable to a Ross filter (5, 6) utilizing two filters composed of two elements of adjacent atomic number whose thicknesses were adjusted so that the transmitted spectra were identical for all wave lengths except for the narrow band between the respective K absorption edges. Therefore, relatively sharp Bragg reflections of each crystallographic plane became possible in the low-angle region in addition to the reflections caused by the characteristic Kα radiation of the tube. These low-angle reflections repeated the powder pattern or single crystal spots given by the characteristic radiation, but at spacings on the film corresponding to the average wave length of the narrow band between the above-mentioned K absorption edges.

In the first column of Table I, the *d*-values of the low-angle lines of α-Cds were calculated for Cu Kα radiation ($\lambda = 1.541$ Å) since they were obtained in powder diagrams using Ni filtered radiation from a Cu tube (Fig. 1). This follows the procedure used in

[1] Manuscript received April 20, 1955.

TABLE I. *d-Values of the low-angle lines of* CdS *caused by absorption of part of the white radiation in the sample and film emulsion*

d in Å* $\lambda = 1.541$Å	Observed relative intensity	d in Å† $\lambda = 0.475$Å	Indices	Hexagonal α — CdS d in Å	Observed relative intensity
11.5	3	3.54	$10\bar{1}0$	3.55	8
10.5	7	3.23	0002	3.33	4
			$10\bar{1}1$	3.13	9
7.98	3	2.45	$10\bar{1}2$	2.43	5
6.75	5	2.08	$11\bar{2}0$	2.06	10
6.19	4	1.91	$10\bar{1}3$	1.89	7
—	—	—	$20\bar{2}0$	1.782	5
5.70	4	1.754	$11\bar{2}2$	1.755	7
5.32	−1	1.64	$20\bar{2}1$	1.723	5
—	—	—	0004	1.673	−1
—	—	—	$20\bar{2}2$	1.575	3
4.92	−1	1.515	$10\bar{1}4$	1.516	1
4.58	1	1.41	$20\bar{2}3$	1.396	5
—	—	—	$21\bar{3}0$	1.351	4
—	—	—	$21\bar{3}1$	1.323	6
—	—	—	$11\bar{2}4$	1.299	2
4.11	1	1.265	$10\bar{1}5$	1.263	−1
—	—	—	2132	1.255	6
—	—	—	$20\bar{2}4$	1.225	−1
—	—	—	$30\bar{3}0$	1.191	4
3.74	1	1.151	2133	1.156	6

* The d-values of the observed low-angle lines as determined for $\lambda_{CuK\alpha}$.

† The d-values of the same lines as determined for an average wave length between the K absorption edges of Cd and Ag.

the previous paper (1). In the third column, however, the same low-angle lines of α-CdS (Ni filtered radiation from a copper tube) were calculated using a wave length of 0.475 Å. The d-values obtained with this average wave length can be compared with the d-values of hexagonal α-CdS which are shown in the fifth column. A comparison shows that the low-angle lines can be indexed by the hexagonal unit cell dimensions of α-CdS if the correct wave length is used.

The layer lines appearing in the low-angle region of single crystal rotation photographs (1) could be explained by the same effect. In general, there was good agreement between the d-values for all observed lines, although the relationship of the intensities did not seem to be maintained in all cases. This variation and the deviation of the position of $(20\bar{2}1)$ in the low-angle region were probably caused by other overlapping diffraction effects (3) in this region of the film. The intensity changes may also have been a result of the change in value of the atomic scattering factor of Cd near the absorption edge.

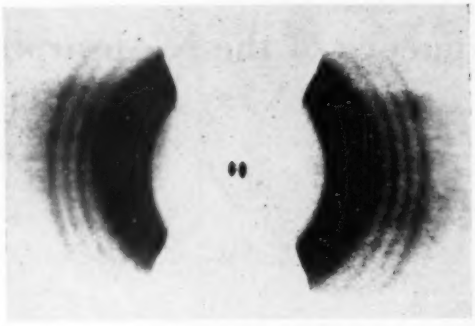

FIG. 1. Low-angle lines in a powder diagram of α-CdS caused by absorption effects of the white radiation in the sample and film emulsion.

At 24 kv the minimum wave length in the emission spectrum of the x-ray tube is above 0.5 Å and the low-angle diffraction effects should disappear. This phenomenon was verified on a sample which had shown the effect at 40 kv. Similar calculations made on the position of the low-angle lines in x-ray diagrams of CdSe and CdO showed the same agreement between the calculated and observed d-values. The occurrence of the low-angle diffraction effects on photographic films also could be avoided by first reflecting the characteristic radiation of the tube on a crystal monochromator.

Differences in intensities and sharpness of the low-angle lines (1) were probably caused by changes in the radiation condition of the x-ray tube and by variation of the amount of sample in the camera, which explains the absence of the effect in some of the reported diagrams. No other polymorphic modification or stacking faults, as discussed tentatively in a previous communication, seemed to be present in the vapor-phase-grown CdS crystals. Mechanical deformation faulting, observed by grinding, should change the appearance of the pattern equally in the low-angle region and in the part produced by the characteristic Cu radiation.

Any discussion of this paper will appear in a Discussion Section to be published in the June 1956 JOURNAL.

REFERENCES

1. F. SCHOSSBERGER, *This Journal*, **102,** 22 (1955).
2. H. P. KLUG AND L. E. ALEXANDER, "X-Ray Diffraction Procedure," p. 381, J. Wiley & Sons, Inc., New York (1954).
3. A. BAXTER AND J. C. M. BRENTANO, *Phil. Mag.* **24,** 473 (1937).
4. R. BROOKS, *Brit. J. Appl. Phys.*, **2,** 76 (1951).
5. P. A. ROSS, *Phys. Rev.*, **28,** 425 (1926).
6. P. KIRPATRICK, *Rev. Sci. Inst.*, **10,** 186 (1939); *ibid.*, **15,** 223 (1944).

Preparation of High-Purity Thorium by the Iodide Process[1]

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ABSTRACT

Preparation of massive thorium of high-purity, in lots of several hundred grams each, by the van Arkel–de Boer (iodide) process is described. Substantial reduction in the nonmetallic content of the deposits over that of the feed material was obtained. Optimum conditions for deposition were determined.

Introduction

The object of this work was the preparation of massive thorium metal[2] of high purity and, more particularly, of metal low in nonmetallic constituents. Although a number of processes[3] described in the literature yield metal low in metallic impurities, few of these processes lead to the freedom from nonmetallic impurities that is attainable by the iodide method. In the van Arkel–de Boer method, as described in this paper, thorium metal of high purity was prepared in lots of several hundred grams. By using a feed material low in metallic impurities and employing the iodide process to remove a substantial amount of the nonmetallics, a high-purity product was obtained.

Experimental

Preparation of Feed Material

In the work reported here, thorium, furnished by the AEC, was used as a feed material. Heavy chips were cut from sections of an ingot or rolled plate, using a shaper without lubrication of the tool. Prior to use, the feed was degreased, washed with distilled water, and dried. Approximately 4 kg of cleaned thorium chips was placed in the annular space between the inner wall of a Pyrex deposition bulb (Fig. 1B) and a perforated molybdenum retainer.

Preparation of Deposition Vessel

A V-shaped "starting filament" of iodide-thorium wire, 0.64 mm in diameter and about 115 cm in overall length, was attached to ¼-in. diameter tungsten supporting electrodes by means of molybdenum tie wires. In order to prevent premature burnout of the filament during the deposition operation, sufficient tie wire was provided to insure a tapered junction between starting wire and electrode. A bridged quartz ring was attached to the lower end of the filament by means of fine tungsten wire. This ring served the dual functions of keeping the filament under slight tension and of preventing it from coming in contact with the metal feed retainer. With the tied filament (Fig. 1A) centrally located in the deposition vessel, the Pyrex electrode cap was sealed to the bulb. The sealed deposition bulb (Fig. 1C) was next attached to an all-glass vacuum system through a short length of constricted tubulation.

Outgassing and Iodination

The deposition vessel was outgassed at 510°C for 24 hr. At the end of this period, the residual pressure in the bulb was usually of the order of 10^{-4} mm of mercury. During outgassing, a side arm, containing about 10 g crushed, resublimed iodine, was kept under refrigeration. The outgassed deposition unit and the attached side arm containing the iodine were sealed off from the vacuum system and the bulb was cooled to 260°C, the temperature at which iodination was carried out. The arm containing the iodine was allowed to warm to room temperature and the iodine was slowly vaporized into the deposition vessel by gentle heating with a gas torch. The product of the iodination reaction was canary yellow thorium tetraiodide, observable on the bulb walls and feed after the vessel had cooled to room temperature. Subsequent to iodination, the exhaust tubulation was sealed off at the constriction, and the

[1] Manuscript received March 20, 1955. This paper was prepared for delivery before the Chicago Meeting, May 2 to 6, 1954. Work on the paper was performed under AEC Contract (W-7405-eng-92).

[2] Thorium, a metal of possible interest as a nuclear fuel, is relatively nonreactive when freshly prepared, being silvery in appearance when cut or polished. Although its natural radioactivity is somewhat greater than that of ordinary uranium, it has never been considered dangerous. Thorium compounds, principally the oxide, are used industrially in such applications as luminous gas mantles, for special purpose refractories, and in electron-tube cathodes. The fine metal powder is sometimes used in electron tubes as a getter. While some fires have occurred, owing to the pyrophoric nature of the powder, thorium is generally considered to be nonhazardous to work with.

[3] W. C. Lilliendahl, "Rare Metals Handbook," Chapter 23, (C. A. Hampel, Editor), Reinhold Publishing Corporation, New York (1954). A description of the Ames Process for the preparation of thorium is not available.

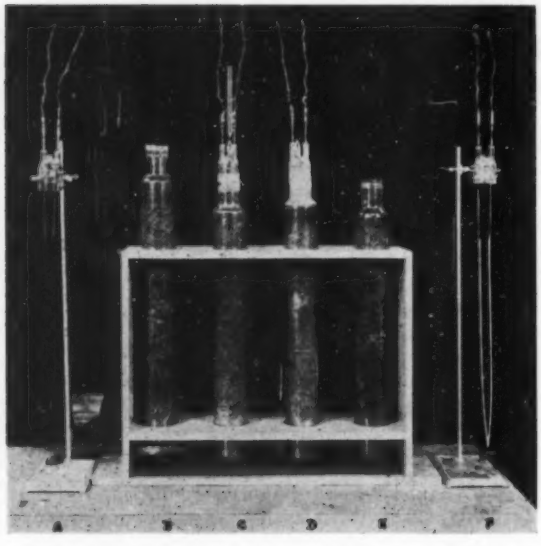

FIG. 1. Iodide thorium at various stages of processing

finished bulb (Fig. 1D) was placed in the deposition furnace.

Deposition

It was found that deposition took place most readily when the externally measured bulb temperature was in the range 455°–485°C. Hence, the deposition furnace was provided with sectionalized windings which could be controlled individually to maintain the desired temperature range. Radiation-shielded thermocouples were attached to the deposition vessel at the center of each furnace section. A cooling coil, made of thin-walled copper tubing, was embedded in the furnace insulation in order to remove the large amount of heat developed in the central portion of the bulb during the later stages of the run as the power input to the filament increased.

Sixty-cycle a-c power was supplied to heat the filament. Voltage leads were attached to the electrodes at the supply-lead junctions.

Since it was difficult to determine the temperature of the filament, correct operating conditions were reached by an indirect means. The voltage applied to the filament was increased in steps until onset of deposition was indicated by an increase in current while the voltage was held at a particular value. On the assumptions (*a*) that the emissivity and resistivity of the filament remain constant, and (*b*) that no heat is lost from the filament by conduction through the supporting electrodes, it can be shown that the filament temperature remains constant as the symmetrical cross section increases uniformly, if the following relation is satisfied:

$$I^{1/3}E = K$$

where I = current (amp), E = applied voltage (v), and K = a constant.

It was found that deposition would usually begin if E and I were such that $K = 0.43$/cm of filament length, and that burnout of the filament rarely occurred if K was equal to or less than 0.63/cm. Hence, initially, E and I were adjusted to give $K = 0.43$/cm and then the voltage was maintained at a constant value until $K = 0.63$/cm was reached. Subsequently, the voltage was decreased as the current increased in order to maintain constant "K." Runs were terminated when the current reached values of the order of 100 amp, since the bulb temperatures could not be restricted to the desired level at higher current owing to the large amount of heat radiated from the filament.

After termination of deposition, the electrode-cap seal was cracked with a hot wire, the finished filament was removed (Fig. 1E and 1F) and trimmed, and the feed was washed with tap and distilled water, and dried prior to the succeeding run. The cap was cleaned, the old tie-sections were removed, and a new filament was attached to the supporting electrodes.

Factors Influencing Deposition and Characteristics of Iodide Thorium

A representative V-shaped thorium "crystal bar" prepared during the course of the work is shown in Fig. 1F. This filament was 0.62 cm in diameter and 112 cm in over-all length. Approximately 200–250 g of metal was prepared per run, depending on the conditions under which deposition took place. The average deposition rate was about 10 g/hr for this length of filament. The deposited metal consisted of bright, rather loosely to well-knit, columnar grains, which extended radially from the center to the outside of the bar. The cross sections of the grains varied from a fraction of a square millimeter to several square millimeters in area. Individual grains

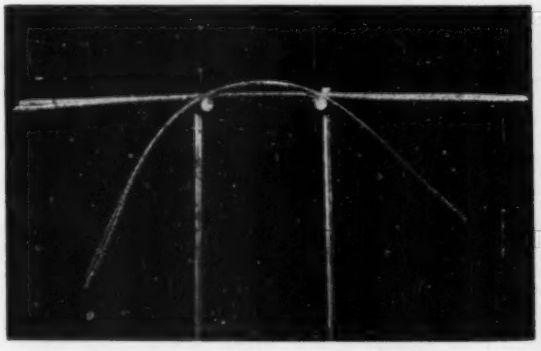

FIG. 2. Comparison of rapidly (straight) vs. less rapidly (curved) deposited iodide thorium crystal bar.

were quite ductile and could be bent sharply through an angle of 180° without fracture.

In general, it can be said that rapidly deposited iodide metal tends to be more closely knit and has somewhat smaller grain size than does metal deposited less rapidly, even though the apparent temperature of the bar is the same in the two cases. Fig. 2 illustrates the degree of compactness achieved in two crystal bars, one of which was deposited at a considerably greater rate than the other, and, hence, possessed greater stiffness.

Similar experiments with other refractory metals have shown that smoother deposits could be obtained if the filament temperature is high enough. However, the low tensile strength of thorium precluded operation at sufficiently elevated filament temperatures to achieve such results. Thus, larger crystal bars tend to pull apart under their own weight during deposition and possess rough, rather coarsely crystalline surfaces.

As in the case of both titanium and zirconium, one of the most important single factors influencing the deposition rate of thorium in the van Arkel–de Boer process was the temperature of the deposition vessel and its effect on the vapor pressure and stability of the iodides. At the iodination temperature used in this work (260°C), thorium tetraiodide was formed. The tetraiodide was relatively stable in the presence of excess metal at any temperature below about 500°C. At temperatures above 500°C, however, it reacted with excess metal to form the less volatile lower iodides. In the preparation of thorium metal by the van Arkel–de Boer process, prolonged operation at high bulb temperatures resulted in the tie-up of iodine as relatively nonvolatile lower iodides. The rate of filament growth decreased as the feed material was covered with a film of lower iodides, and deposition ultimately stopped. This could be avoided by operating at bulb temperatures in excess of 600°–610°C, at which temperatures the lower iodides disproportionate. However, Pyrex glass softens in this temperature range; thus, deposition of thorium from the lower iodides in Pyrex equipment was not feasible.

Since the deposition rate increased with the bulb temperature, up to the temperatures at which the formation of lower iodides took place, there was an optimum bulb temperature for Pyrex apparatus. This optimum was found experimentally to be in the range 455°–485°C.

When using Vycor, silica, or metal deposition vessels, it was possible to raise the bulb temperature sufficiently to secure deposition from the lower iodides. In some deposition runs in Pyrex, radiation from the filament was sufficient to permit local overheating which led to the formation of lower iodides, as evidenced by black lustrous deposits on the walls of the deposition vessel. For this reason, also, it became necessary to terminate the runs when the crystal bars had grown to an appropriate diameter.

TABLE I. *Comparison of impurity levels of thorium feed metal and iodide thorium prepared from this feed*

Material	Element, % by wt		
	Carbon	Oxygen	Nitrogen
Thorium feed metal.....	0.115	0.110	0.029
Thorium crystal bar.....	0.020	<0.01	<0.01

TABLE II. *Comparison of room temperature mechanical properties of AEC and iodide thorium*

Property	AEC thorium	Iodide thorium
Hardness, VHN.....	80	40
Ultimate tensile strength, psi.....	30,000	20,000
Reduction in area, %.....	48	60

Discussion

The extent of reduction of nonmetallic impurities afforded by the iodide process is illustrated in Table I, which shows the carbon content reduced to about $\frac{1}{6}$ that of the feed, oxygen to less than $\frac{1}{10}$, and nitrogen to less than $\frac{1}{3}$.

The mechanical properties of thorium were considerably influenced by the nonmetallic impurity content. Decreasing hardness, increasing ductility, and lower tensile strength usually go hand in hand with increasing purity.

As further evidence of the reduction in the nonmetallic content which the iodide process gives, Table II indicates comparative values for the hardness, tensile strength, and reduction in area of both the AEC-feed material and the iodide thorium prepared from it. The hardness value is markedly lower.

It should be pointed out that thorium is apparently less sensitive to oxygen and nitrogen than are titanium and zirconium, two other Group IV metals frequently prepared by the iodide process. Although the reduced oxygen and nitrogen content undoubtedly has some effect on the mechanical properties of iodide thorium, other work has shown that lower carbon content is primarily responsible for the observed decrease in hardness.

Any discussion of this paper will appear in a Discussion Section to be published in the June 1956 Journal.

Liquidus Curves for Aluminum Cell Electrolyte

II. Ternary Systems of Cryolite-Alumina with Sodium Fluoride, Sodium Chloride, and Aluminum Fluoride[1]

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ABSTRACT

Liquidus curves for those parts of the systems molten at 1050°C have been determined by means of cooling curves and visual examination of the cooling melt. The system cryolite-alumina-aluminum fluoride is incomplete due to the high volatility of the latter component. The binary systems of cryolite with sodium fluoride, sodium chloride, and aluminum fluoride gave, respectively: eutectic point at 882°C, 40% sodium fluoride; eutectic point at 734°C, 68.5% sodium chloride; peritectic point at 734°C, 30% aluminum fluoride; and eutectic point at 693°C, 40% aluminum fluoride (compositions in weight per cent). Diagrams for the three ternary systems have been made.

Introduction

In a previous paper (1) liquidus curves for the binary system cryolite-alumina were reported and compared with earlier data. The object of this paper is to present liquidus curves for the ternary systems cryolite-alumina with sodium fluoride, sodium chloride, and aluminum fluoride. Only scanty data on these systems were available, and they were obtained solely by the cooling curve method, which gives erroneous results for the binary system on the alumina side of the eutectic point.

Primary freezing points were determined for those parts of the systems molten at 1050°C by the cooling curve method and by visual examination of the cooling melt.

Materials

Hand-picked natural cryolite containing no visible impurities was crushed to pass 150 mesh. It contained 0.02% iron, 0.03% silicon, 0.02% magnesium, and 0.01% lead. The alumina was Alcoa A-10, which had a loss on ignition at 1000°C of 0.17% and contained 0.06% sodium, 0.04% iron, and 0.03% silicon. The aluminum fluoride was produced by vacuum distillation from Baker's reagent-grade hydrate. It contained 0.09% iron, 0.02% silicon, 0.03% manganese, and 99% aluminum fluoride (based on total fluorine content). The sodium fluoride, which contained no free alkali, and the sodium chloride were Baker's reagent-grade.

Method

The apparatus and methods used in this investigation were as described for the system cryolite-alumina (1). As for this system, primary freezing points were determined by the cooling curve method when the first appearance of crystals, as observed through a telescope, corresponded with the primary break in the cooling curve. This was so for the three binary systems of cryolite with sodium fluoride, sodium chloride, and aluminum fluoride, and for the corresponding ternary systems containing alumina on the cryolite side of the eutectic line. Cooling rates of 1–3°C/min were used.

On the alumina side of the eutectic line in the ternary systems there was no break in the cooling curve corresponding to the first appearance of crystals in the melt, and the primary break occurred at an appreciably lower temperature. Here the primary freezing points were obtained by the visual method, i.e., by determining the temperature at which crystals first appeared in the slowly cooling melt. For final determinations, rates of cooling of less than 0.1°C/min were used. The failure to obtain a corresponding break in the cooling curve is attributed to the sluggishness with which the crystals form and to the steepness of the liquidus curves.

The platinum, 10% rhodium-platinum thermocouples were checked regularly at the freezing point of pure sodium chloride. With melts containing aluminum fluoride the determinations were made as rapidly as possible to minimize changes in composition due to evaporation.

Accuracy

Results obtained by the cooling curve method for the binary and ternary systems containing sodium fluoride or sodium chloride are not in error by more than 3°C. The limit of error for results obtained by the visual method on these ternary systems, i.e., on the alumina side of the eutectic line, is estimated to be 5°C. No significant error due to changes in

[1] Manuscript received May 31, 1955. This paper was prepared for delivery before the Cincinnati Meeting, May 1 to 5, 1955.

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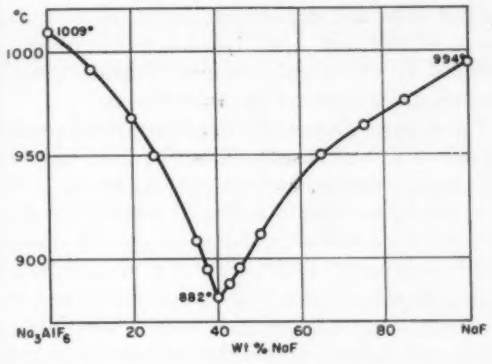

FIG. 1. Liquidus diagram for cryolite-sodium fluoride

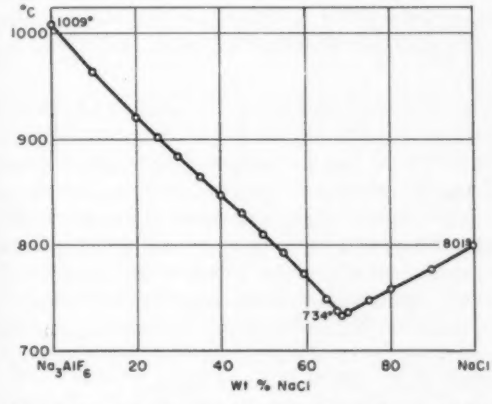

FIG. 2. Liquidus diagram for cryolite-sodium chloride

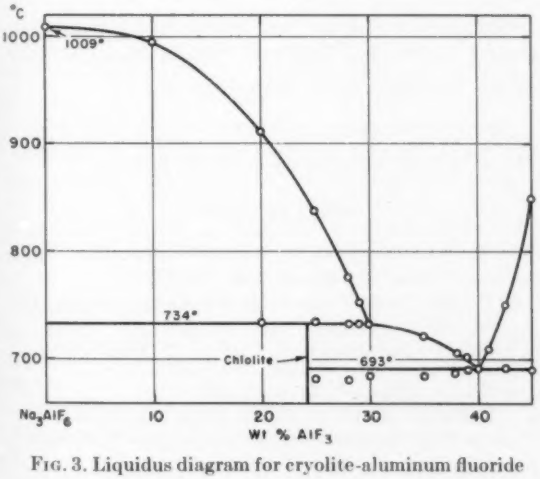

FIG. 3. Liquidus diagram for cryolite-aluminum fluoride

composition was revealed by repeated measurements on the same melt or by weight loss.

For the system cryolite-aluminum fluoride, the loss by evaporation during a determination was less than 1% for aluminum fluoride contents up to 40%, and the limit of error of the results in this range is 3°C. This applies also to the system cryolite-

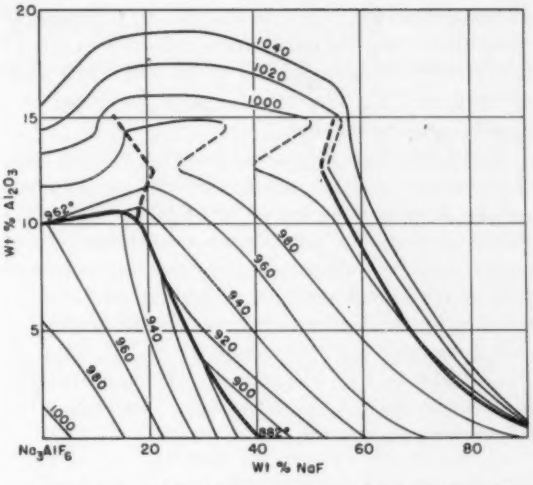

FIG. 4. Liquidus diagram for cryolite-alumina-sodium fluoride.

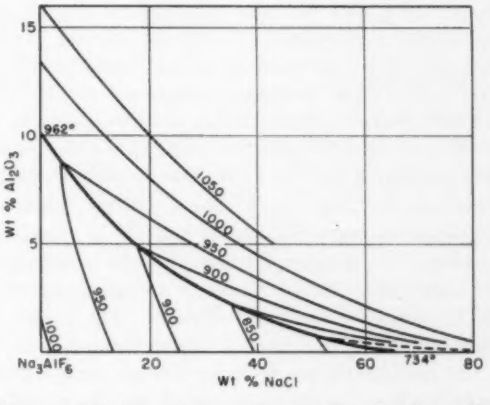

FIG. 5. Liquidus diagram for cryolite-alumina-sodium chloride.

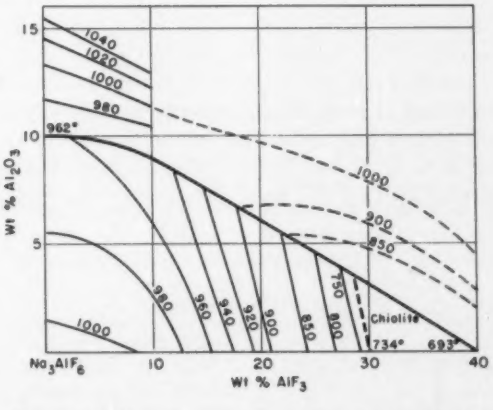

FIG. 6. Liquidus diagram for cryolite-alumina-aluminum fluoride.

alumina-aluminum fluoride on the cryolite side of the eutectic line. On the alumina side of the eutectic line at 10% aluminum fluoride, the estimated limit of error is 5°C. The other results for these two systems are less reliable.

In the course of the measurements reported here, the freezing points of sodium chloride, cryolite, and sodium fluoride were found to be 800°, 1006°, and 991°C, respectively. Subsequent measurements with a thermocouple calibrated at the freezing points of pure silver and samples of aluminum and copper certified by the National Bureau of Standards gave slightly higher values, namely 801° ± 0.5°, 1009° ± 1°, and 994° ± 1°C, respectively. Hence the results reported for the binary and ternary systems are believed to be slightly low.

Results

The liquidus diagram for cryolite-sodium fluoride (Fig. 1) has a eutectic point at 882°C and 40% sodium fluoride (weight per cent). The early results of Fedotieff and Ilyinskii (2), and of Lorenz and co-workers (3), which are not shown, are in fair agreement with those of the present work. Petit (4) reports 885°C for the eutectic temperature. Cryolite-sodium chloride (Fig. 2) has a eutectic point at 734°C and 68.5% sodium chloride. No data have been published previously on this system. Cryolite-aluminum fluoride (Fig. 3) has a peritectic point in the liquidus curve at 734°C and 30% aluminum fluoride, corresponding to the peritectic melting of the compound chiolite. There is a eutectic point at 693°C and 40% aluminum fluoride. The results of Fedotieff and Ilyinskii are in fair agreement.

The liquidus diagram for cryolite-alumina-sodium fluoride (Fig. 4) is based on those for cryolite-alumina (1) and cryolite-sodium fluoride, and on sections taken at 1, 5, 10, 12.5, 15, and 17.5% sodium fluoride. Pure sodium fluoride would dissolve 0.01% alumina, but not 0.05%, at 1100°C. There is a eutectic line joining the eutectic points of the two binary systems. Another eutectic line joins it at 18% sodium fluoride, but its position is only tentatively established. A peritectic line runs from 15% alumina, 55% sodium fluoride to the sodium fluoride corner. The data of Vajna (5), covering sodium fluoride contents up to 15%, were obtained by the cooling method only and did not reveal the eutectic line. Those of Fedotieff and Ilyinskii, for solutions of alumina in the cryolite-sodium fluoride eutectic mixture, are in error for the same reason.

The liquidus diagram for cryolite-alumina-sodium chloride (Fig. 5) is based on those for the corresponding binary systems, and on sections taken at 0.5, 2, 5, and 10% alumina and at 10 and 20% sodium chloride. Pure sodium chloride would not dissolve 0.01% alumina at 1100°C. There is a eutectic line joining the eutectic points of the two binary systems. The only other data on this system are those of Henry and Lafky (6), who determined the percentage of alumina which would dissolve in cryolite containing up to 20% sodium chloride on prolonged stirring at a given temperature. They are in only rough agreement with those of the present investigation.

The liquidus diagram for cryolite-alumina-aluminum fluoride (Fig. 6), which has been only partially determined, is based on those for cryolite-alumina and cryolite-aluminum fluoride, and on sections at 5% alumina and 10% aluminum fluoride, respectively. There is a eutectic line joining the eutectic points of the two binary systems and a peritectic line corresponding to the decomposition of chiolite. The data of Vajna covering aluminum fluoride contents up to 15% are in approximate agreement on the cryolite side of the eutectic line.

Acknowledgment

The authors wish to acknowledge the assistance of Miss Anne Fischer and Mr. Leon Villeneuve who carried out many of the measurements.

Any discussion of this paper will appear in a Discussion Section to be published in the June 1956 Journal.

REFERENCES

1. N. W. F. Phillips, R. H. Singleton, and E. A. Hollingshead, *This Journal*, **102**, 648 (1955).
2. P. P. Fedotieff and Vl. Ilyinskii, *Z. anorg. Chem.*, **80**, 113 (1912).
3. R. Lorenz, A. Jabs, and W. Eitel, *ibid.*, **83**, 39 (1913).
4. G. Petit, *Compt. rend.*, **234**, 1281 (1952).
5. A. Vajna, *Alluminio*, **22**, 635 (1953).
6. J. L. Henry and W. M. Lafky, Paper presented at the American Chemical Society Meeting, New York (1954).

Discussion Section

OXIDATION OF IRON-MOLYBDENUM AND NICKEL-MOLYBDENUM ALLOYS (pp. 7–15)

CATASTROPHIC OXIDATION OF SOME MOLYBDENUM-CONTAINING ALLOYS (pp. 16–21)

S. S. Brenner

N. J. GRANT[1]: Unfortunately, the author was entirely unaware of the research conducted on the mechanism of this type of oxidation and published elsewhere.[2]

There has been considerable duplication of effort; fortunately, the mechanism proposed by Mr. Brenner agrees in substance with that proposed in the two papers cited and therefore strengthens the prior theoretical considerations.

A high concentration of the contaminating element (Mo, V, W, Bi, or Pb) was also found at the metal-oxide interface by x-ray and chemical analysis in these publications. The oxidation reaction was determined to take place at the metal-oxide interface and atmospheric oxygen was shown to have direct contact with this interface. In addition, it was found necessary to have a liquid oxide present for accelerated oxidation to occur. The temperature increase at the interface as a result of the oxidation reaction which is hypothesized by the author was actually measured and recorded.

Based on this evidence, a mechanism of accelerated oxidation had been proposed in which the liquid oxide reacted with the metal to form the metal oxide plus a suboxide and was illustrated by means of x-ray diffraction studies of the oxide present. The suboxide is subsequently regenerated by atmospheric oxygen which has direct contact with the metal-oxide interface and the accelerated oxidation process continues.

S. S. BRENNER: I presume Dr. Grant refers mainly to the paper on catastrophic oxidation. I cannot agree with him that there was a considerable degree of duplication of effort, although there was necessarily some overlapping. The main purposes of the paper were: (*a*) to show the effect of stepwise changes of composition on the oxidation of some prepared molybdenum alloys, (*b*) to show how catastrophic oxidation is initiated in these alloys, and (*c*) to clarify further the growth of the bulk oxide which is separated from the metal surface by the liquid oxide phase.

The author was aware of the publications hypothesizing a liquid oxide layer at the metal-oxide interface and the accompanying oxidation-reduction process. References to some of these publications were made at the beginning of the paper. Similarly the temperature increase at the liquid oxide-metal interface was not presented as an hypothesis by the author but was used rather to clarify the growth process of the bulk oxide.

Perhaps more detailed references would have avoided this misunderstanding.

This Discussion Section includes discussion of papers appearing in the JOURNAL of The Electrochemical Society, **102**, No. 1–6 (January–June 1955). Discussion not available for this issue will appear in the Discussion Section of the June 1956 JOURNAL.

[1] Dept. of Metallurgy, Massachusetts Institute of Technology, Cambridge, Mass.

[2] F. C. MONKMAN AND N. J. GRANT, *Corrosion*, **9**, 460 (1953); also, A. DeS. BRASUNAS AND N. J. GRANT, *Trans. Am. Soc. Metals*, **44**, 1117 (1952).

THE ELECTRIC ARC AS A CIRCUIT ELEMENT

T. E. Browne, Jr. (pp. 27–37)

GEORGE W. VINAL[3]: The paper by T. E. Browne, Jr., recalls to mind the series of papers on the electric arc by Professor Walter G. Cady and several of his graduate students, including H. D. Arnold and myself. These are not mentioned by Dr. Browne. In some particulars these earlier papers, published in 1907 to 1909, anticipate results reported by Dr. Browne. As an example, Fig. 1 in his paper is practically identical with Fig. 1 in the paper "On the Electric Arc Between Metallic Electrodes" by Cady and Vinal[4] and its translation.[5] Other papers of Professor Cady's series on the arc appeared in these journals.

T. E. BROWNE, JR.: No attempt was made to present a complete bibliography with this paper, but the author appreciates the mention by Dr. Vinal of the additional early papers on the subject.

POLARIZATION STUDIES OF COPPER, NICKEL, TITANIUM, AND SOME COPPER AND NICKEL ALLOYS IN THREE PER CENT SODIUM CHLORIDE

H. B. Bomberger, F. H. Beck, and M. G. Fontana (pp. 53–58)

CECIL V. KING[6]: The authors call attention to the reduction of oxygen in aerated solutions and of hydrogen ions in all solutions as responsible for the cathodic polarization observed. It may be of interest to make quantitative calculation of the oxygen diffusion current and the hydrogen ion concentration polarization to be expected.

The reversible potential, vs. the saturated calomel cell (SCE), for oxygen reduction, is given by

$$E = 1.228 - 0.246 - 0.06\,p\mathrm{H} + 0.015 \log p_{O_2} \quad \text{(I)}$$

with $p_{O_2} = 0.2$ atm and $p\mathrm{H} = 7$, $E = +0.55$ v; if $p\mathrm{H} = 11$, $E = +0.31$ v. Oxygen is reduced at less positive and all negative potentials, hence, at any potential considered here.

The oxygen diffusion current is given by

$$i_d = 4FDc/\delta \text{ amp/cm}^2 \quad \text{(II)}$$

[3] 12 E. Stanworth Drive, Princeton, N. J.

[4] W. G. CADY AND G. W. VINAL, *Am. J. Sci.*, **28**, 89 (1909).

[5] *Physik. Z.*, **10**, 569 (1909).

[6] Dept. of Chemistry, New York University, New York, N. Y.

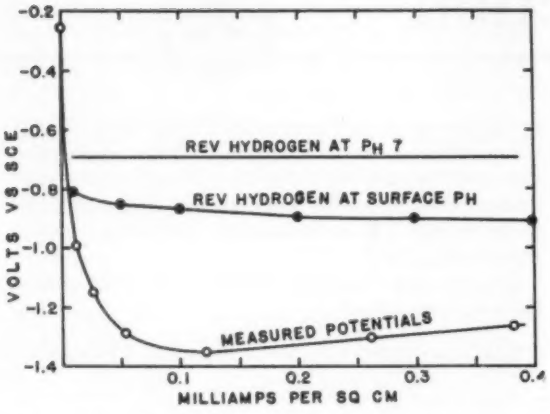

FIG. 1. Cathodic polarization of copper in 3% NaCl

where **F** is the faraday, D the diffusion coefficient, c the concentration in moles/cm³, δ the effective diffusion layer thickness. The solubility of oxygen at 0.2 atm and 30°C is about 2×10^{-7} moles/cm³, the diffusion coefficient is 1.9×10^{-5} cm²/sec, and, at the rate of solution flow used (50 ft/min or 25 cm/sec), δ is known to be about 1.0×10^{-2} cm.[7] Putting these values in equation (II), $i_d = 1.5 \times 10^{-4}$ amp/cm². It is interesting that approximately this value is found for copper and titanium, a somewhat smaller value for brass; the Cu-Ni alloys give modified curves, and oxygen reduction is completely suppressed on nickel.

No matter whether oxygen or hydrogen ion is being reduced, if the solution has no buffer capacity, the cathode surface solution becomes alkaline at very small current densities. Assuming a bulk pH near 7 and no buffer action, the surface hydroxyl concentration is given by:[8]

$$C_{OH^-} = 10^3 \frac{i}{\mathbf{F}} \frac{\delta}{D} \text{ moles/liter} \qquad \text{(III)}$$

Fig. 1 shows (*a*) the reversible hydrogen electrode potential at pH 7; (*b*) the reversible hydrogen electrode potential at pH values calculated from equation (III); and (*c*) cathode potentials of copper in deaerated solution as measured by the authors, all as functions of current density. The figure suggests that the observed polarization consists of three terms: (*a*) a very small current, probably much less than 10^{-5} amp/cm², completely polarizes the open circuit corrosion potential and converts the cathode to a hydrogen electrode; (*b*) surface pH changes account for 0.12 to 0.22 v in the current range used; and (*c*) the remainder, 0.4 to 0.5 v, is due to hydrogen overpotential.

M. G. FONTANA: Dr. King's interesting calculations serve to point out, among other things, significant differences between the various materials employed as cathodes in their rates of oxygen reduction and hydrogen overpotentials. These two polarization characteristics determine largely the effect a given cathode material will have on current flow in a corrosion cell in a solution such as the one employed, i.e., in a solution in which hydrogen ions and oxygen are the only reducible agents. Concentration changes have an important but somewhat less effect.

M. J. PRYOR[9]: Although polarization curves determined by the application of small constant currents from an external battery have been used widely for the interpretation of corrosion data, the accuracy with which these curves represent continuations of the local-cell polarization curves on a corroding specimen has never been fully established. This probably reflects the inherent difficulty of measuring actual local-cell polarization curves and, also, the fact that some of the assumptions made in estimating these local cell polarization curves, e.g., from observed potentials and calculated currents, are at least questionable in nature.

However, the authors and others[10] have suggested that cathodic polarization curves determined by the application of constant currents may be useful in determining maximum corrosion currents flowing during galvanic corrosion (*See* Bomberger, Beck, and Fontana's Fig. 12). In order to investigate this suggestion, D. S. Keir[11] is currently comparing polarization curves obtained (*a*) by the application of constant currents from an external battery and (*b*) by shorting dissimilar metal electrodes through a variable series resistance, with current, potential, and weight loss data obtained on the appropriate galvanic couples under otherwise similar conditions. The first method of determining polarization curves is essentially similar to that used by the authors except that an auxiliary platinum electrode was not used. The second method is probably more representative of conditions existing during galvanic corrosion since both the potential and current can vary until steady-state conditions are achieved. To date it has been found that, in normal sodium chloride solutions containing dissolved air, much flatter cathodic polarization curves having less well defined breaks are obtained on copper, steel, and aluminum by employing the emf of the galvanic couple as the potential source than are obtained by using constant currents from an external battery. Thus, only a gross qualitative similarity exists between the two sets of cathodic polarization curves. Furthermore, cathodic polarization curves obtained using the emf of a galvanic couple as the potential source are useful for making predictions concerning the potential and current during galvanic corrosion, whereas the polarization curves obtained using the constant currents from an external battery are not.

Reasons for the inability of applied current cathodic polarization curves to reflect the observed behavior of a galvanic couple may be as follows.

In the applied current determinations of cathodic polarization curves, the current is purposely held constant. Therefore, if the oxygen in the region of the cathode becomes depleted the potential of the cathode must change abruptly in the negative (less noble) direction so that hydrogen ions can be reduced. However, should the oxygen

[7] C. V. KING, *J. Am. Chem. Soc.*, **57**, 828 (1935).
[8] C. V. KING, *This Journal*, **102**, 193 (1955).

[9] Dept. of Metallurgical Research, Kaiser Aluminum & Chemical Corp., Spokane, Wash.
[10] W. A. WESLEY, *Am. Soc. Testing Materials, Proc.*, **40**, 690 (1940).
[11] Labs., Kaiser Aluminum & Chemical Corp., Spokane, Wash.

at the cathode become depleted during galvanic corrosion (or also during local cell corrosion) the corrosion current will almost certainly decrease temporarily, thereby permitting oxygen to diffuse from the bulk of the solution back to the solution/cathode interface. This will tend to maintain a higher concentration of oxygen in the region of the cathodes to reduce cathodic polarization. Evidently the same sequence of events can occur during determination of polarization curves using the emf of the galvanic couple as the potential source.

Therefore, it should be realized that both local-cell corrosion and galvanic corrosion are self-regulating processes, whereas determination of cathodic polarization curves by means of the application of constant applied currents from an external emf is not. Although the authors attribute the difference between their measured and calculated current values for the copper-steel couple to contamination of the copper cathode by iron corrosion products, it should be realized that these two experiments were performed under two entirely different sets of conditions.

M. G. Fontana: Dr. Pryor correctly notes that the use of constant currents from an external source does not yield information as applicable for galvanic cell studies as is obtained in the direct study of specific galvanic cells, since the current in a galvanic cell has a tendency to change. Changes in current imply nonsteady-state conditions that can be due to a number of variables, such as, polarization of the partner electrode, film growth, and temperature and environmental changes. In a carefully controlled experiment a corrosion cell should eventually acquire and maintain a constant current so that the polarization of its cathode should be quite similar to that of another cathode polarized with constant current under otherwise identical conditions. Any differences that may exist then can be attributable to surface conditions acquired during the unsteady-state history of the cells.

This, of course, is difficult to demonstrate. In such a study, sufficient time must be allowed and skill exercised to develop steady-state conditions. The choice of accompanying anodes is important since their polarization characteristics will affect the behavior of the test cathode, and contamination of the solution by salts from the anode must be avoided.

Constant currents from an external emf can be used to advantage in polarization studies, depending on the specific objectives. For example, data can be obtained under conditions that are readily defined, and the polarization characteristics of the electrode under study are not influenced by the peculiarities of the accompanying electrode; this gives information that should be more fundamental to the material under study.

NITRIDES OF CHROMIUM AND CHROMIUM-TITANIUM ALLOYS

New Film-Type Resistance Elements

E. R. Olson, E. H. Layer, and A. E. Middleton (pp. 73–76)

Donald Caplan and Malcolm J. Fraser[12]: After treating Cr powder in ammonia, x-ray diffraction analysis by the authors showed the presence of Cr_2N and CrN. This indicates that each granule consisted of a case of CrN surrounding a core of Cr_2N which means, in turn, that equilibrium had not been attained in the ten-min treating time. Otherwise, the powder would have been entirely CrN. It is most probable, however, that the evaporated films of Cr, since they were only 200 to 1500 Å thick (approximately 80 to 600 atomic distances) were totally converted to CrN. (We have found, for instance, that, even in specimens three orders of magnitude thicker, the nitride layer thickens at a rate in excess of 10^4 Å/10 min at 1050°C.) It follows that in all cases the authors were examining single-phase films and, therefore, their suggestion that Cr_2N has a lower resistivity than CrN is not justified. The variation in electrical characteristics of the film observed by the authors might be related to variations with treating temperature of the Cr/N ratio in the CrN.

We have found, as did the authors, that, in the temperature range 950° to 1250°C, Cr is nitrided to CrN by ammonia. Single-phase films of the lower nitride, Cr_2N, could be prepared, if required, in an atmosphere of dissociated ammonia over this same temperature range.

E. R. Olson: We appreciate the interest of and comments by Mr. Caplan and Mr. Fraser on our studies. We have been following their work with great interest and consider their findings of considerable value to our work.

The questionable presence of Cr_2N in our resistor films was brought to our attention some time ago through examination by electron diffraction methods of films nitrided at 1100° and 900°C. The studies revealed the presence of CrN and Cr but no Cr_2N. Investigations are currently getting under way in which correlation of electrical properties with Cr/N ratio will be studied. Preparation of both Cr_2N and CrN-type structures will be attempted to establish the effects of structure variations as well as nitrogen content on the electrical characteristics.

Incidentally, although it was not specifically stated in the article, the nitriding time for the powders was 60 min. Even this, however, may not have been sufficient time to reach equilibrium.

THE CRYSTALLOGRAPHIC DEPENDENCE OF THE OXIDATION POTENTIAL OF SOLID COPPER

W. E. Tragert and W. D. Robertson (pp. 86–94)

M. E. Straumanis[13]: The results obtained on copper by the authors agree with those obtained on zinc some decades ago[14]: no appreciable differences in equilibrium potentials, as measured on different single Zn crystal planes, could be detected, and, under hydrogen, the potential of the single planes was equal to that of zinc amalgam. If there were some small differences then they were due to reasons of secondary nature. However, crystal planes dissolving in the electrolyte showed different dissolution potentials.[15] This behavior of metallic crystals can be explained well.[16]

The plane of electrolytic growth of Cu-crystals is the

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[13] Dept. of Metallurgy, School of Mines and Metallurgy, Rolla, Mo.

[14] M. Straumanis, *Z. physik. Chem. A*, **147**, 161, Table I (1930).

[15] M. Straumanis, *ibid.*, **147**, 161, Table II (1930).

[16] M. Straumanis, *ibid.*, **156**, 150 (1931).

111-plane.[17] This again agrees very well with the authors' statement that the plane with the most stable potential is the 111-plane. Thus, single Cu-crystals are electrolytically built up and decomposed over the 111-plane.

RESISTANCE AND POLARIZATION IN A STORAGE BATTERY

E. Willihnganz (pp. 99–101)

J. J. LANDER[18]: When the negative plate of the lead-acid cell is discharged, an unusual polarization curve is observed. This consists of a very rapid drop occurring in times which may be measured in fractions of a second, followed by a gradual recovery which may take seconds or minutes. This was explained by Dr. Willihnganz[19] as being due to supersaturation of the solution in the neighborhood of the electrode with lead ions which are being discharged into solution. The voltage recovery occurs because the supersaturation is at least partially relieved by precipitation of lead sulfate on the electrode.

That such a process is quite possible is very easily demonstrated by mixing two solutions which will produce a solution supersaturated with lead sulfate and observing the time for turbidity to occur. Moreover, such an explanation is consistent with data which have been accumulated in our laboratory in studies of negative plate polarization.

During the time that the lead ion is establishing supersaturation in the surface layer and before the rate of precipitation becomes appreciable, diffusion into the body of the solution can take place and this process will limit, initially, the build-up in lead ion concentration at the surface. Therefore, using the equation for linear diffusion

$$\Delta C = \frac{2It^{\frac{1}{2}}}{\pi^{\frac{1}{2}} n\mathbf{F}AD^{\frac{1}{2}}}$$

and assuming the applicability of the Nernst equation, the build-up in polarization at the discharging lead electrode can be calculated. Results are shown in Table I as a function of current density. For comparison, the last column shows how polarization would build up if the polarization process resulted from the depletion of the sulfate ion concentration at the surface of the electrode.

TABLE I. *Polarization in volts*

log t*	Current Density			
	170 ma/cm²	1.7	0.16	170 ($SO_4^{=}$ depletion)
−6.0	0.07	0.01		
−4.0	0.10	0.038	0.012	
−2.0	0.13	0.066	0.040	
0		0.095	0.068	0.001
+1.0				0.005
+2.0				0.032

* t in seconds.

[17] G. TAMMANN AND M. STRAUMANIS, *Z. anorg. Chem.*, **175**, 131, 135 (1928).

[18] Naval Research Lab., Washington, D. C.

[19] E. WILLIHNGANZ, *Trans. Electrochem. Soc.*, **79**, 253 (1941).

The interesting feature of this table is the extreme rapidity with which polarization values of some magnitude can be established, and this for a Faradaic process at quite ordinary current densities. Obviously, this results from the very low concentration of lead ions in solution at the start (about 9×10^{-9} moles/cc), so that the passage of but fractions of coulombs can result in a manyfold increase in the lead ion concentration in the surface layer. If the supersaturation process actually occurs in the discharge of the lead electrode, then it must be reckoned with in making polarization measurements and interpreting them. For example, one can readily see that the usual methods of making resistance measurements would result in high values.

Dr. Willihnganz is probably quite correct in ascribing his high apparent resistances at the lower frequencies to a "pseudocapacitance." It seems questionable, however, that his results must be disassociated from changes in the lead ion activity and that, therefore, the negative plate reaction must take place in two steps.

It has already been indicated for one of his experimental conditions, namely the pulse discharge with the cell at rest, that the lead ion concentration could be important. Because he is directing his attention to the electrode surface rather than the solution layer, he concludes that the size and duration of the pulse is sufficient to cause only a minor disturbance in the double layer. That is to say, if the Nernst theory is applicable here, it is the change in concentration of ions in the solution layer which determines the voltage change. It can readily be calculated, using his estimated area and measured current and time, that, if the lead ions produced were constrained to remain in a 10 Å thick layer in the surface electrolyte, the concentration would be increased sixtyfold. This is equivalent to a polarization of 50 mv. Of course, diffusion must occur and, if the linear diffusion equation is applied to the same data, the concentration change in the solution at the electrode surface is calculated to result in a polarization of 1.2 mv which is somewhat greater than the measured value of 0.5 mv but is obviously large enough to account for it. With the cell at rest, it is practically immaterial whether this is a charge or discharge pulse because, for a charge pulse where concentration at the electrode surface is limited by diffusion of lead ions to the surface, a polarization of 1.35 mv is calculated. Therefore, it is possible that two of the experimental conditions can be explained on the basis of lead ion activity changes.

It may be argued that, because the cell was given a 2% discharge, sufficient lead sulfate nuclei were present to allow rapid crystallization of the lead sulfate and so the supersaturation effect would be eliminated. Our data show that the effect is indeed reduced when lead sulfate crystals are present to start with, but it requires something like 50% discharge of a flat plate to eliminate the effect entirely.

For the conditions where the pulse is superimposed on a charge or a discharge current, the situation seems much less clear. However, the argument, that, because a millionfold change in lead ion activity is apparently involved, the change in lead ion activity cannot be responsible for the polarization voltage, does not seem to be justified, be-

cause, inasmuch as a pseudocapacitance is involved, the same argument clearly can be leveled at any other mechanism of the same type which might be proposed. In view of the foregoing and the remarkable similarity of the traces, it seems just as reasonable to say that the lead ion concentration is responsible for the polarization in all cases. Furthermore, in the search for another mechanism it would be necessary to find a Faradaic process the polarization characteristics of which would be as sensitive to minute quantities of current as is the straightforward reaction. If such were found, then the original explanation for the negative plate polarization on discharge would be in considerable doubt, to say the least.

The millionfold figure does not seem to be unquestionable. It is not stated exactly in the paper to what the 0.1 and −0.1 v polarization values correspond. Presumably they are the steady-state differences in voltage between the cell on charge or on discharge vs. the open circuit voltage, i.e., the sum of the polarization at both plates and the internal resistance drop. The value of −0.1 would be about right for a discharge at the 4-hr rate (25 amp). If so, then, on discharge, 0.025 v of the total is due to internal resistance. Our data indicate that the polarization at the positive plate is greater than that at the negative after the negative has settled down, but, even if the polarization were equal at both plates, the value at the negative would be only 0.037. This means that the change in concentration at the negative under these discharge conditions would be seventeenfold. A similar condition at the charging overvoltage of 0.1 v would result in a total change of 17 × 40, or about seven hundredfold.

E. Willihnganz: The comments of J. J. Lander show a difference of opinion concerning the presence of a concentration gradient of lead ions at the surface of a lead electrode when current is flowing. We did not mean to imply that such a gradient does not exist, or that it is not important. We did try to eliminate this gradient as completely as possible so that we could measure the internal resistance of a storage battery and get a number which meant actual electrical resistance. Consequently, our experimental conditions were considerably different from those usually encountered in studying electrode reactions.

For example, these test conditions are considerably different from those used in polarography. In a polarographic analysis, conditions are chosen to emphasize the importance of the diffusion gradient, while we tried to minimize it.

Where the mechanism of an electrode reaction is being studied, there is certainly a possibility that the concentration gradient is the end result of a series of reactions. It is the steps which precede the establishment of a concentration gradient which we feel are not clearly understood, and our pulse discharge data were merely an attempt to point out the possible existence of a problem.

Mr. Lander's criticism concerning the omission of an *IR* correction from the calculation is correct, but not important. The term "polarization" is used in the following fashion: A polarization of −0.1 v is the difference in potential between a negative plate equilibrium in sulfuric acid and a similar electrode when current is flowing at a constant rate. With a discharge current of 25 amp, with a cell resistance of 0.001 ohm, and on the assumption that half of this resistance can be ascribed to the negative plate, the 0.1 v figure we used should be corrected to 0.088 v, while, during charge at 1 amp, the corrected polarization becomes 0.0995 v. If these values now are inserted in the Nernst equation and if it is assumed that at equilibrium the electrolyte contains 9×10^{-9} moles/cc of lead ions, we find that during charge the lead ion concentration has dropped to 1.5×10^{-12}, while during discharge it has increased to 2.2×10^{-5}.

The pulse polarization amounts to about 0.5 mv for either of the above lead concentrations. Again applying the Nernst equation, this corresponds to a 4% change in concentration of lead ions. This leads to a discrepancy. It seems impossible for a 0.01 microcoulomb/cm² pulse to produce a 4% change in concentration at the interface, irrespective of whether the initial concentration was 10^{-5} or 10^{-12} moles/cm². This is one of the reasons for believing that the pulse voltage is not controlled by the concentration of lead ions in solution, but rather by the composition of the double layer on the lead surface.

Mr. Lander's calculations of polarization voltages, using Fick's law and assuming a concentration gradient, can be criticized from two standpoints. First, he is talking about a different order of magnitude of current density from our work; second, he is using a figure for the surface area in a battery which we feel is not reliable within an order of magnitude. We estimated the effective electrode area of the sponge lead in a storage battery from the measurements of Falk and Lange. This was merely an approximation to learn the order of magnitude of the disturbance of the electrode surface. The use of this estimate of area to calculate diffusion gradients and voltages seems to put more trust in the estimate than it deserves.

Our major reason for suspecting something other than a diffusion gradient lies in the measurements of Falk and Lange at high frequencies. In the range of 1000 to 20,000 cycles, their values for the apparent capacitance and parallel resistance do not appear to fit the rather simple picture of a double-layer capacitance and a concentration gradient. For this reason, we believe that the lead electrode deserves further study to work out the charge and discharge mechanism.

THE EXTRACTIVE METALLURGY OF ZIRCONIUM BY THE ELECTROLYSIS OF FUSED SALTS

III. Expanded Scale Process Development of the Electrolytic Production of Zirconium from K_2ZrF_6

Bertram C. Raynes, Edward L. Thellmann, Morris A. Steinberg, and Eugene Wainer

(pp. 137–144)

James C. Schaefer[20]: You said that the graphite middle section of your cathode extended beneath the surface of the molten bath. Some zirconium probably deposits on the graphite section and, if so, suggests the possibility of the formation of ZrC by interaction of the Zr deposited with the graphite. Have you found any evidence of such taking place?

[20] Republic Steel Corp., Cleveland, Ohio.

MORRIS A. STEINBERG: Some zirconium does deposit on the graphite section of the cathode which extends into the melt. This portion of the deposit is contaminated with carbon and ZrC to some extent and is generally discarded. However, this amounts to only 1–2% of the total deposit.

ROBERT C. WADE[21]: 1. How much K_2ZrF_6 is lost by washing out the salts in the cathode deposit? What is the yield of Zr based on K_2ZrF_6?

2. How many washes are necessary to get a halide-free product?

3. What is the halide content (%) of the final powder?

MORRIS A. STEINBERG: 1. The deposits contain about 1–2% by weight of zirconium as salts. This is equivalent to 2–4% of the total available Zr. The average yield of metal based on K_2ZrF_6 is 85–90%.

2. For a deposit containing 4000 g Zr, 90–100 l of water in about 20 washes were used. This volume may be reduced by one half or more by recycling the wash water.

3. No accurate data are available on halide contents of the powder. However, the final wash water gives no detectable precipitate on addition of $AgNO_3$.

PRELIMINARY INVESTIGATION OF HAFNIUM METAL BY THE KROLL PROCESS

H. L. Gilbert and M. M. Barr (pp. 243–245)

G. M. BUTLER[22]: 1. Carborundum Metals Company is faced with reduction of several thousand pounds of HfO_2 to sponge. I asked if the authors' observation, that $HfCl_4$ reacted more readily with H_2O than did $ZrCl_4$, could be due to the small scale and relatively crude nature of the small chlorinator used.

Mr. F. E. Block[23] said that the difference was real and troublesome—$HfCl_4$ being more reactive and harder to treat to remove.

2. I commented that preliminary Hf sponge production experiments at Carborundum Metals Company tended to confirm the authors' observation that buttons melted from the sponge were quite hard and difficult to machine. Purity requirements were not as high as for reactor-grade zirconium.

H. L. GILBERT: Mr. Butler's question concerning the reactivity of hafnium tetrachloride with water is one which has been given much thought and effort in our laboratory. We believe from our experience that there is greater initial reactivity in the case of hafnium tetrachloride and can state that, when zirconium and hafnium tetrachlorides are subjected to the same purification step of vacuum treatment and sublimation, the zirconium tetrachloride is transferred in the pure anhydrous form while hafnium tetrachloride seems to be associated with a series of oxygen-containing compounds which either transfer by sublimation or decompose and reform with the net result that the sublimed hafnium tetrachloride is not oxygen free. These compounds are active over an extended range from below to considerably above the sublimation temperature of hafnium tetrachloride. Our most exacting laboratory effort has not produced an oxygen-free hafnium tetrachloride.

[21] Metal Hydrides Inc., Beverly, Mass.

[22] The Carborundum Co., Niagara Falls, N. Y.

[23] Nonferrous Metals Branch, Northwest Electrodevelopment Lab., U. S. Bureau of Mines, Albany, Oreg.

S. J. MORANA[24]: Has any particular difficulty been observed in maintaining a constant briquet level by using the closed feeding system described in the slide?

H. L. GILBERT: Mr. Morana's question concerning the maintenance of the proper briquet level in the chlorinator is quite in order. We found it necessary to determine the briquet level at least once during each shift, by inserting a graphite probe through the chlorinator top.

RESISTANCE STUDIES ON VARIOUS TYPES OF DRY CELLS

Richard Glicksman and C. K. Morehouse (pp. 273–278)

The authors make the following correction of an error in their original paper. On p. 275, under the heading *Discussion*, the first sentence should read: "Vinal (1) has pointed out that, as far back as 1885, Preece found that the resistance of a cell was less when measured at high current drains than when measured at low current drains."

J. J. COLEMAN[25]: This paper, like all others that I know on the subject of the internal resistance of dry cells, ignores a basic difficulty. Whatever the "equivalent circuit" is for a dry cell, it certainly is not a simple resistor. In fact, a condenser in parallel with a resistor is probably not sufficiently complex to represent a dry cell—or even one of the electrodes.

To make clear what recognition of a dry cell as a complex network means, I invite your attention to what happens if the experimenter replaces the dry cell with an assembly consisting of a dry cell in parallel with a condenser. This adds one more complication to an already complicated network. In other words this assembly is not much more complicated than the dry cell itself. Suppose that the experimenter makes his measurements on this assembly. What conclusions can he draw?

In the first place, it is apparent that any determination of the impedance of this assembly by alternating current of a single frequency will tell us nothing about the internal resistance of the dry cell. Speaking crudely we can say the difficulty is that we do not know how much current goes through the dry cell and how much goes through the condenser.

In recognition of this problem various experimenters have measured the "instantaneous" potential drop which results in a direct current being sent through the cell. Turning our attention to the dry cell in parallel with a condenser again, it is clear that this provides no solution. While the condenser does not affect the flow of current after a steady state is reached, it is an important factor during the first few milliseconds of discharge.

A very short pulse of direct current has many of the aspects of alternating current. It will, for example, pass through a condenser.

Moreover, it is easy to demonstrate that we are concerned with a real, practical difficulty. After prolonged discharge the bobbin in a dry cell is permeated throughout with a hard mass of dry crystals. Obviously, the resistance of the web of electrolyte has increased tremendously.

In such a cell, alternating current or a pulse of direct current can travel to the edge of the bobbin entirely as an

[24] The Beryllium Corp., Reading, Pa.

[25] Burgess Battery Co., Freeport, Ill.

electronic current and can be converted into an ionic current at the surface of the bobbin by an action which is analogous to that of a condenser, or a storage battery, or both. No prolonged flow of direct current, on the other hand, can be maintained in this way.

Perhaps a quantitative example will be helpful. Suppose that the web of black has a resistance of 1 ohm and the web of electrolyte has the same resistance in an undischarged cell. One would guess that the resistance of the bobbin would be ½ ohm and this turns out to be a very good approximation. Suppose now that the resistance of the web of electrolyte goes to infinity. A flow of direct current lasting several minutes is impossible. So far as any practical use of the cell is concerned, this one factor—without regard to the condition of the manganese dioxide or zinc—is sufficient to prevent the flow of useful current. Practically speaking, it is meaningful to say that the internal resistance itself has risen to infinity.

On the other hand, the resistance to alternating current or to a pulse of direct current is 1 ohm.

Any experimenter who ignores these difficulties is likely to conclude that the increase of internal resistance plays a minor role in the fall of potential during discharge. In some cases such a conclusion would be correct, but in many cases it is wrong, and in no cases can it be proven by the method described in the present paper.

RICHARD GLICKSMAN AND C. K. MOREHOUSE: It is true, as Dr. Coleman says, that a dry cell cannot be simply represented as a resistor; however, his suggestion that it would be better represented as a capacitor in parallel with a resistor, as shown in Fig. 1*a*, does not fully explain the experimental results.

A dry cell with such an equivalent circuit would give an oscillographic curve similar to that shown in Fig. 1*b* when it goes from a closed to open circuit condition, i.e., the cell voltage would increase exponentially as soon as the current was interrupted. However, our measurements show an oscillographic curve with a large discontinuity (Fig. 1*d*), indicating that the major portion of the resistance is not effectively bridged by a capacitor. This would correspond more closely to the equivalent circuit pictured in Fig. 1*c*.

The fact that the discontinuity represents over 80% of the total increase indicates that the capacity could only effectively parallel a small part of the resistance. Furthermore, a substantial part of the remaining 20% voltage increase with time is probably due to the decay of concentration and activation polarization processes which would give a voltage-time curve similar to the exponential recovery curve of a capacitor. Therefore, we would conclude that the capacitance parallels only an inappreciable part of the resistance, and that we are getting a fairly accurate measurement of the internal resistance of a dry cell.

Dr. Coleman also suggests the possibility of the electrolyte being converted into dry crystals as a result of prolonged discharge. This condition may exist in completely run-down cells, but it does not apply here, where D-size cells were discharged at a 0.200-amp constant current drain for 8 hr. The cell is by no means dry after such a discharge, and we believe that the resistance of the electrolyte increases only slightly during the course of normal discharge, and its value is certainly finite.

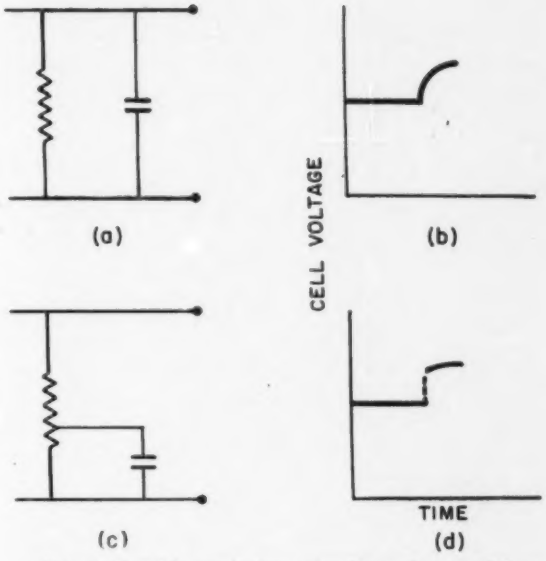


FIG. 1. Possible equivalent circuits and potential recovery curves of a Leclanché dry cell.

Although there are many difficulties involved in measuring the internal resistance of dry cells, it is believed that the results obtained from our measurements are valid. They show that the change in internal resistance as a cell is discharged accounts for only a small percentage of the total voltage drop and that other factors are more important in contributing to the gradual fall of potential with time in the Leclanché cell.

RECENT INNOVATIONS IN THE CONTROL AND OPERATION OF ZIRCONIUM REDUCTION FURNACES

F. E. Block and A. D. Abraham (pp. 311–315)

MORRIS EISENBERG[26]: Have you or your group attempted to work out the mechanism and chemical kinetics for the Mg-$ZrCl_4$ reaction on the basis of the operational data for the batch process?

F. E. BLOCK: The reaction rates discussed in this paper are actually average rates since the reaction is nonuniform in nature. Actually, the reaction occurs at small centers around the inside edge of the crucible and it may shift rapidly to one or more different locations. Also, the rate of zirconium chloride sublimation is nonuniform and the concentration of chloride vapors in the retort atmosphere varies throughout the reaction. For these reasons kinetic data could not be calculated on the basis of the batch operation.

A METALLURGICAL EVALUATION OF IODIDE CHROMIUM

D. J. Maykuth, W. D. Klopp, R. I. Jaffee, and H. B. Goodwin (pp. 316–331)

W. H. SMITH[27]: This paper is a welcomed contribution to those engaged in a study of the metallurgy of chromium.

[26] Stanford Research Institute, Stanford, Calif.

[27] Research Lab., General Electric Co., Schenectady, N. Y.

Several of the statements made by the authors, however, conflict with results obtained at this laboratory and elsewhere. The first is in regard to the effect of nitrogen on the room temperature ductility of chromium. Our work indicates that the ductility of chromium is more adversely affected by small amounts of nitrogen than any other single impurity. It has been found that less than 0.01% by weight of nitrogen in annealed chromium can raise the bend transition temperature well above room temperature. Slightly more, 0.02% nitrogen, can be tolerated in cold-worked chromium before the bend transition temperature exceeds room temperature. These findings confirm those of Wain, Henderson, and Johnston[28] who set the limit of nitrogen in cold-worked metal at 0.02% and a limit of 0.001% in annealed material if room temperature ductility is to be maintained. I do not believe that any data presented in your paper are specific enough to warrant the conclusion that nitrogen contents up to 0.032% have no apparent effect on bend ductility.

Regarding your conclusions on the effect of sulfur, I should like to make the following comments. Alloys of chromium containing 0.1% sulfur prepared by arc melting have been bend tested in the as-cast condition. The transition temperature was less than 100°C which is in the range expected for the base composition used, without sulfur. We have not tried to fabricate these alloys. Your poor results on rolling suggest that sulfur may render chromium hot short. It would be interesting to know if the authors found any adverse effects of sulfur on the bend ductility of as-cast chromium.

D. J. Maykuth: Our work did not include a study of the specific effects of nitrogen on the ductility of chromium. With the exception of a single sample, each of the chromium sheets evaluated contained 0.005% nitrogen or less, and, as noted in our paper, variations in nitrogen content below this value had no apparent effect on the room temperature ductility of chromium. However, one ingot of commercial electrolytic chromium, which contained 0.032% nitrogen, 0.26% oxygen, 0.005% carbon, and 0.014% sulfur, was fabricated to sheet and evaluated in bend tests in the wrought condition. Samples of this sheet showed an average ductile-to-brittle transition temperature of −15°C, a temperature which compares favorably with iodide chromium sheet containing about the same amount of carbon and sulfur, but appreciably less nitrogen and oxygen. Our statement that nitrogen variations from 0.001 to 0.032% have no apparent effect on bend ductility was based on these observations

The results of Mr. Smith's bend tests on as-cast chromium-sulfur alloy samples were noted with interest. Since we did not investigate the as-cast bend ductility of any of our samples, we are not able to offer any additional information on this subject.

[28] H. L. Wain, F. Henderson, and S. F. M. Johnston, *J. Inst. Metals*, **83**, 133 (1954).

PREPARATION OF TITANIUM BY FLUORIDE ELECTROLYSIS

M. A. Steinberg, S. Carlton, M. E. Sibert, and E. Wainer (pp. 332–340)

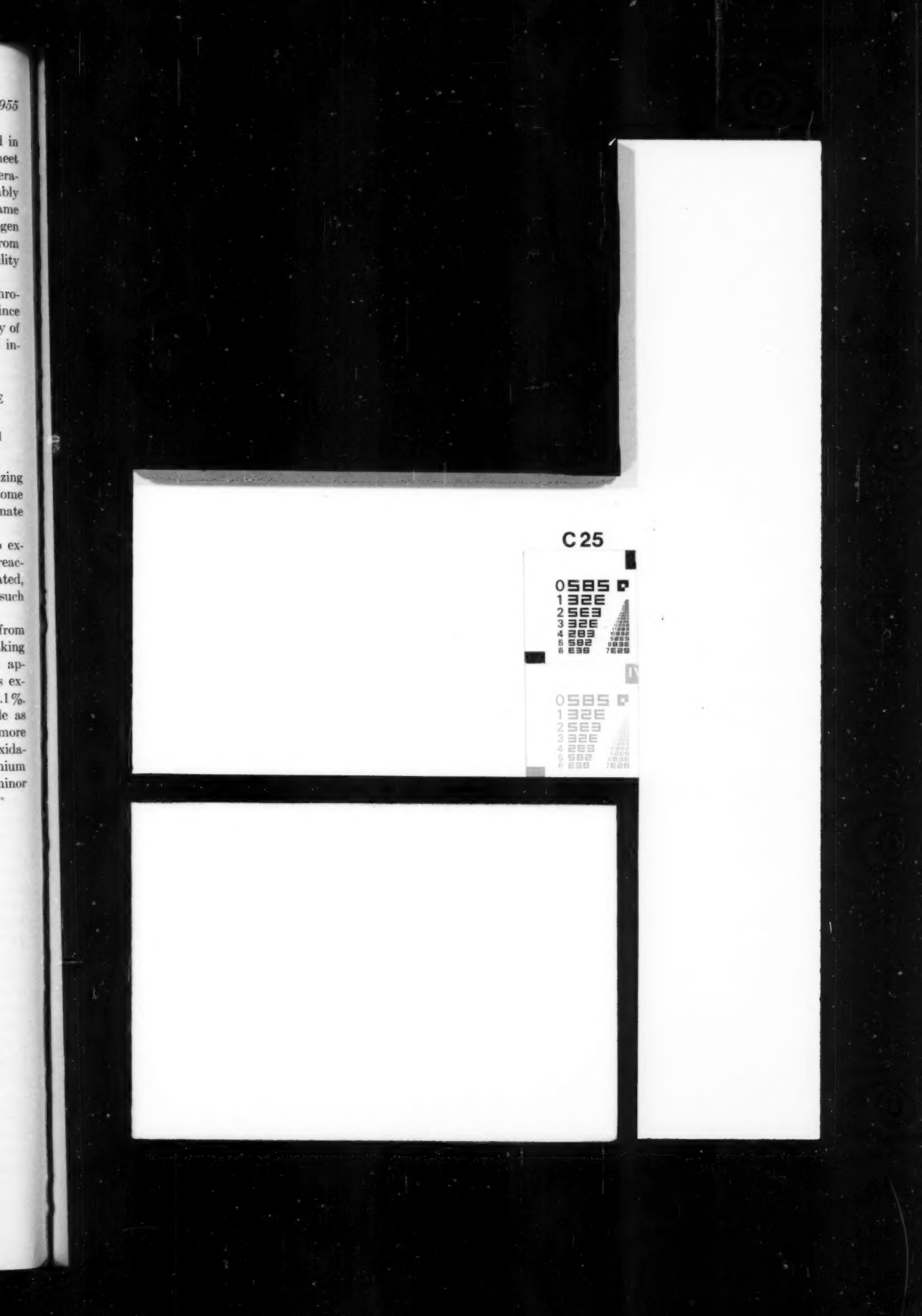
James C. Schaefer[29]: 1. You spoke of recrystallizing the K_2TiF_6 from hot water. Are you sure that some $Ti(OH)_4$ does not form by hydrolysis and contaminate your salt?

2. You also spoke of a low efficiency, but had no explanation for same. Don't you think that there is a reaction between the Ti and some of the Cl_2 that is liberated, and also have you considered the solubility of Ti in such a molten bath?

M. E. Sibert: 1. The K_2TiF_6 was recrystallized from hot water, but the solution was distinctly acid, making hydrolysis negligible. Any $Ti(OH)_4$ so formed would appear as an insoluble phase (TiO_2). No difficulty was experienced in obtaining insoluble contents of less than 0.1%.

2. Chlorination of deposited titanium is negligible as evidenced by the type of crystal growth obtained. A more tenable explanation for efficiency losses is anodic reoxidation of reduced [Ti(II) and Ti(III)] ion species. Titanium is soluble in the K_2TiF_6-NaCl melt, but this is also a minor factor in this case.

[29] Republic Steel Corp., Cleveland, Ohio.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